FILTER CAKE REMOVAL OF BARITE WATER-BASED MUD

BY

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Dedicated to

My Mother,

My Father,

My Wife,

My Children,

My Brothers,

My Sisters, and

My Family

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In the name of Allah, Most Gracious, Most Merciful. All praise is to Almighty Allah who donated me intelligence, experience and capability to complete my dissertation work and blessing of Allah be upon His prophet Mohammed.

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LIST OF ABBREVIATIONS

P_m	:	Mud Pressure
P_f	:	Formation Pressure
WBM	:	Water Based Mud
HPHT	:	High Pressure High Temperature
SEM	:	Scanning Electron Microscopy
XRD	:	X-ray Diffraction
XRF	:	X-Ray Fluorescence
CT scan	:	Computerized (or Computed) Tomography
DTPA	:	Diethylenetriamine Pentaacetic Acid
EDTA	:	Ethylene-Diaminetetraacetic Acid
HEDTA	:	Hydroxyethyl Ethylenediamine-Triacetic Acid
DOCTA	:	Dioxaoctamethylene Dinitrilo Tetraacetic Acid
KOH	:	Potassium hydroxide
NaOH	:	Sodium hydroxide
K_2CO_3	:	Potassium carbonate
$CHKO_2$	:	Potassium formate
KCl	:	Potassium chloride

g/l	:	gram per liter
PHV	:	Number of Pore Hole Volumes required to dissolve the filter cake
RDA	:	Rotating Disk Apparatus

ABSTRACT

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The removal of barite filter cake is a challenging problem because the conventional filter cake removal treatments that use hydrochloric acid (HCl) or chelating agents were ineffective in dissolving barite-containing filter cakes. Barite, or barium sulfate, is insoluble in water and acids such as HCl, formic, citric, and acetic acids. Also barite has very low solubility in chelating agents such as Ethylene diamine tetra acetic acid (EDTA) and Diethylene triamine penta acetic acid (DTPA).

The present study focuses on the development of a new formulation to remove the barite filter cake. The removal formulation consists of chelating agents such as Diethylene Triamine Penta acetic Acid (DTPA), converting agent or catalyst, and a polymer breaker (Enzyme). Solubility tests of industrial barite and solids collected from de-sanders during well flow back were conducted to develop barite-removing solvent. Actual barite drilling fluid samples were collected from the field during drilling a high pressure high temperature deep gas well. The performance of the designed formulation in removing the filter cake formed was examined by real drilling fluid samples collected during drilling operations using High Pressure High Temperature cell (HPHT).

Based on the result of this work, it can be stated that the filter-cake-removing formulation dissolved more than 90% of the filter cake formed by real barite drilling fluid in a single

stage within 24 hours. The removal formulation consists of high pH potassium base DTPA of 20% wt concentration, enzyme as a polymer degrading agent, and one of the following converting/catalytic agents: potassium carbonate, potassium formate, or potassium chloride. The use of converting agents increased the barite solubility from 67% to 90%.

ملخص الرسالة

الاسم الكامل: بدر سالم باجري

عنوان الرسالة: إزالة كعكة الحفر المكونة بسائل حفر البارايت ذو الأساس المائي

التخصص: هندسة البترول

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إزالة كعكة فلتر الباريت هي مشكلة صعبة لأن علاجات إزالة كعكة الحفر التقليدية التي تستخدم مثل حمض الهيدروكلوريك (HCl) أو المركبات مخلبية غير فعالة في حل كعكة الحفر المتكونة بسائل الحفر الذي يحتوي مادة الباريت. الباريت أو كبريتات الباريوم، غير قابل للذوبان في الماء والأحماض مثل حمض الهيدروكلوريك، والفورميك، الستريك وأحماض الخل ممايجعل من يجعل عمليه ترسبه سهل وعملية إزالة صعبة. أيضا الباريت لديه القابلية للذوبان منخفضة في المركبات المخلبيه مثل (EDTA) و (DTPA).

تتركّز هذه الدراسة على تطوير محلول لإزالة الكعكة الحفر المتكونة بسائل الحفر الذي يحتوي الباريت كمركب رئيسي. يحتوي محلول إزالة كعكة الباريت من ثلاثة أجزاء رئيسية: اولاً حمض مخلبي مثل (DTPA) او (EDTA)، ثانياً عامل محفّز لزيادة قابليه ذوبان الباريت في الحمض المخلبي، ثالثاً انزيم مذوب للبوليمر المحيط بالباريت في كعكعة الحفر. تم اجراء اختبارات الذوبانية للباريت باستخدام الباريت المتسخدم كمادة زيادة كثافة سائل الحفر وكذلك تم اختبار قدرة المحلول على ذوبانية المواد المتجمعه من البئر عقب ازالتها سائل الحفر. عينات سائل الحفر المستخدمة في هذه الدراسة لتكوين كعكة الحفر عباره عن سائل حفر تم استخدامها في حفر بئر في الحقل لكي تكون اقرب الى الواقع ولكي تعطي نتائج اكثر دقة. تم فحص أداء محلول إزالة الكعكة باستخدام عينات سائل الحفر الحقلي التي تم جمعها خلال عمليات الحفر باستخدام الضغط العالي خلية درجات حرارة عالية.

اظهرت نتائج هذه الدراسة أن التركيه المستخدمه ذات قدرة على أزاله كعكة سائل الحفر الحاوي على مادة الباريت بكفائة تصل الى 90% خلال فترة زمنية تصل الى 24 ساعة. التجانس بي محتويات محلول ازالة كعة الحفر وهي 20% من المركب المخلبي والانزيم والمحفّز يسمح في باستخدام هذا المحلول في مرحلة واحده. إنّ اضافة المحفز الى تركية ازاله كعكة الحفر المتكونة بالباريت كان له دور فعّال في زيادة نسبة الذوبانيه من 67% الى مايقارب 90% كما سيتم شرحها بالتفصيل في فصول هذه الاطروحة.

CHAPTER 1

INTRODUCTION

In oil and gas drilling operations, it is of major importance to circulate drilling fluid into the wellbore to enhance the efficiency of the drilling operation. When a well is drilled, a drilling fluid is circulated into the hole to contact the region near the drill bit, for a number of reasons including, to cool the drill bit, to carry the rock cuttings away from the point of drilling, and to maintain a hydrostatic pressure on the formation wall to prevent production during drilling. The drilling fluid is also an essential key factor for reducing the risk of formation damage during drilling. Therefore, a drilling mud program contains many tests such as filtration rate and filter cake properties to select the proper drilling fluid additives that yield the standard ranges of the viscosity, filtration rate, etc.

1.1 Drilling Fluid Additives

The drilling fluid chemical additives are designed carefully to prevent fluid losses to the formation by building an effective filter cake that allow for minimum filtration, prevent solid invasions to the formation, and withstand high differential overbalance pressures [1,2]. One of the main fundamental functions of drilling fluid is to suppress high formation pressures and tp prevent blowout especially in gas and deep wells. In order to perform this tasks, there are many weighting materials, including barite, iron oxides, manganese tetraoxide, potassium formate, hematite and calcium carbonate that are used to achieve the

required density of mud slurry. Consequently, the main source of formation damage may be incurred by the weighting material used in drilling fluid. For long horizontal wellbores the drilled solids are ground into smaller particles if they are not properly removed and mixed with drilling mud during mud circulation. Recently, Bageri et al. [3,4] conducted experimental work to measure the properties of the drilling fluid and the filter cake along a horizontal section of a wellbore. They concluded that about 70% to 80% of the mineral composition of filter cake can be attributed to the drilling fluid weighting material and the rest is composed of drilled formation particles.

Barite is a common weighting agent in drilling fluids which has been used for oil and gas applications deep wells. It is preferred over other weighting materials due to its high density that provides adequate weight leading to desired average drilling fluid density with low production costs and ease of handling. Therefore, the interest of this study is to use barite water-based mud.

1.2 Filter Cake

The drilling fluid must counter or suppress formation pressure. Therefore, the drilling fluid has to have enough density to balance formation pressure and keep the wellbore stable. Due the positive difference between the drilling fluid pressure and formation pore pressure the drilling fluid invades the formation and forms filter cake over the formation face [1–8]. Accordingly, Filter cake occurs intentionally during the drilling operations to prevent fluid losses to the formation and allow good circulation for drilling fluids from the bottom hole to the surface. The filter cake composition depends on a well-designed drilling fluids and

additives [2–4,7,9]. The filter cake should allow for minimum filtration, prevent solid invasions to the formation, and withstand high differential overbalance pressures.

The composition of the formed filter cake over the face of the formation depends on the composition of drilling fluid solids additives, properties of the drilling fluid, the dilled formation mineralogy, the differential pressure, and other factors [3–6,10,11]. The filter cake properties are controlled by sources of the mud solids; mud additives and drilled solids. The drilled solids are usually removed using solids control equipment because their presence may degrade the performance of the drilling mud and change the composition of filter cake [4,12]. Correct selection of solids control equipment is crucial to maintain drilling fluid at its desired properties [13–15]. Because all current solid separation methods are either based on size exclusion or gravity, they ignore the chemical composition of the solids. Thus these drilled particles can also be present in the filter cake composition in horizontal wells [3].

In addition to the deposition of drilling mud particles on the formation face around the wellbore, the small particles in the mud invade the formation causing an internal formation damage [7,16,17], as shown in Figure 1. The internal invasion depth depends on many factors such as the pressure deference, formation properties such as pours size and permeability and drilling fluid solids particles [17].

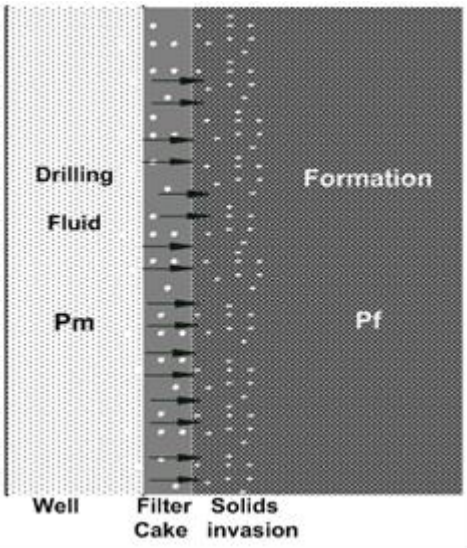


Figure 1 Schematic Diagrams of a Well

To recover hydrocarbons (e.g., oil, natural gas), it is necessary to remove the formed filter cake over the face of the hydrocarbon- bearing formation, such that hydrocarbons can flow from the formation into the wellbore and to the surface. This study focuses on an aspect which was not fully covered in the literature: investigate a solution to dissolve the barite solid where barite solids will be an essential part of filter cake of the barite weighted Water Based Mud (WBM) that commonly used to drill deep wells. The designed formulation will be used later to remove the filter cake formed by barite as weighting material using real drilling fluid samples which collected while drilling operations to control the effect of drilled solids effect.

CHAPTER 2

LITERATURE REVIEW

2.1 Filter cake properties

Various techniques have been developed to have deep understanding of filter cake properties to reduce the challenge facing the industry and to select the proper drilling fluid additives which is the most key factors for successful drilling operation. Such techniques are helpful to design an effective recipe for cleaning wellbore prior to the drilling operation and dissolve the filter cake formed over the face of the permeable formation. The properties such as filter cake thickness, porosity, permeability and mineralogy (chemical composition) are affected by many factors for instant solid content of drilling fluid, drilling fluid properties (density, rheological characteristics, filtration and others) and formation properties (porous size, permeability, pressure and others) [2–4,7–9,16,18–24]. Typically, the most represented method that can simulate the reservoir condition to determine the filter cake parameters is the high pressure high temperature test (HPHT). HPHT filtration test is conducted either on ceramic plate or core sample plug; the preferred one to stimulate the permeable formation properties.

It is noted by several studies that the filter cake thickness is a sensitive function of drilling fluid plastic viscosity, yield point [3,4,9,19]. The dynamic condition (mud shear rate) causes erosion to the filter cake surface and reduces the filter cake thickness [19,24]. The formed filter cake thickness also can be affected by the pressure difference in the well bore

and formation temperature [9]. The generated filter cake may consist two different layers as obtained by Elkatatny et al. [22] using the CT scan technique with different properties. The source of solid content also another key factor affecting the filter cake thickness directly based on the degree of each element such barite, bentonite and XC polymer or indirectly by their impact on drilling fluid rheology characteristics [9,10,25]. Meanwhile the drilled solids adding to mud while drilling operation the filter cake has an effect on the cake thickness [3,4,12]. The particle size of the drilling fluid solids and drilled formation effect the cake thickness as obtained by [19][12][3]. Professionals in the industry usually struggle to get deep understanding of the cake thickness due to its practical and critical contribution in pipe sticking model's calculation. Form the removal point of view, accurate filter cake thickness evaluation leads to relatively correct considered determination of filter cake solid's quantity in the treated section. Accurate calculation of filter cake solid plays a significant role in the calculation of the volume of the removal fluid based on solid liquid ration. The filter cake thickness becomes more significant form the removal point of view due to the heterogeneity of thickness at different parts of the extended reach wells and maximum reservoir contact [3,4,7,16].

Filter cake's porosity and permeability are also other significance parameters to characterize filter cake and evaluate the performance of the designed drilling fluid [7]. Several models and methods were presented in the literature to estimate the permeability and porosity of the filter cake [2]. Through these multi-pronged approaches, despite various factors affects the porosity of the filter cake, it is highly depends on the particle size of the cake solids, filtration properties, the dynamic well condition and pressure drop across the filter cake [2,10,22,24,26–28]. Even with the efforts paid by the drilling fluid experts to

control the porosity of the filter cake, it is known that changing the size and type of the solid particles during the mud circulation and pipe rotation make numerous drawbacks to control and evaluate this parameter. Nevertheless, form the removal aspect, the ratio of the solid content in the filter cake can be obtained from porosity value [7]. This ration can be used in the calculation of the removal volume to dissolve the filter cake solids formed over the target formation as we can see later in the embodiment of this study. The filter cake permeability measured either by using models depend on Dracy's Equation or correlations [22]. Filter cake permeability has to have low value to seal the formation and control the filtration rate; ranging from 10^{-5} Darcies to 10^{-7} Darcies [2][29]. From removal viewpoint, filter cake permeability simultaneously with the porosity play central role by providing an indication about the particle size distribution and arrangement to know the degree of the contact between the removal fluid and the filter cake solids.

Characteristically, several devices have been used to study the filter cake microscopic structure and composition such as scanning electron microscopy (SEM), X-ray diffraction (XRD), X-Ray Fluorescence (XRF), CT scan and others [2,3,27,30–32]. Such tests carried out for deep understanding of the filter cake composition and to improve the drilling fluid additives selection that control filtration and minimize the formation damage. This information is also useful to formulate an effective recipe for removing the filter cake based on the exact chemical compositions of the filter cake solids. The composition of the filter cake and the mineralogy contribute for accurate calculation for the filter cake solid's density where the cake density is one of the main keys to calculate filter cake porosity.

Therefore, to summarize what have been reported previously (descriptions of the main filter cake properties); the filter cake removal success is the product of various influences.

Thus to develop any removal formulation; the influence and expectations of filter cake properties such as thickness, porosity, permeability and chemical composition remain paramount throughout removal process.

2.2 Filter Cake Removal

Drilling fluid typically used several weighting materials (including barite, iron oxides, manganese tetraoxide, potassium formate, hematite, and calcium carbonate, etc.) to achieve the required slurry density to suppress the formation pressure. Barite is a common weighting agent in drilling fluids in deep oil and gas wells. As discussed earlier in this art, the weighting material contributes in average with 70 to 90% weight percent of the filter cake mineralogy [3]. Typically, the filter cake removal formulations gained importance in the last decade where the using of horizontal maximum reservoir contact and extended reach well have been used widely . So this section is presenting recent examples of filter cake removal formulation achieved by investigators for different drilling fluid types;

2.2.1 Manganese Filter Cake

Al Moajil et al (2008) [33] conducted filter cake removal experimental formed by manganese tetraoxide (Mn_2O_3) drilling fluid at 250 psi using HPHT cell statically. The filter cake formed dynamically under 100 rpm in same cell on ceramic disk at 300 °F. They recommended that to enhance the removal efficiency of filter cake generated by Mn_2O_3 two stage of removal should be used. The first stage was using an enzyme with 10% weight prior to the second stage of using the cleaning fluid. The reason for using the first stage

was to break the polymeric coat around the weighting material in the filter cake. They went for two stages filter cake removal process due to the incompatibility of enzyme with the cleaning fluid treatment at low pH and at high temperature as a clear separation of enzyme out of solution was noted. In the first stage 10% weight of enzyme A (as they called it) was socking with filter cake for five days where 24 hours was not adequate and increasing did not help. The cleaning stage was using lactic acid 10% weight; their results showed that the filter cake removal efficiency was 85%. They reported in their study that diethylene triamine pentaacetic acid (DTPA) and Ethylene diamine tetraacetic acid (EDTA) 20% wt% (high pH >12) had poor capability to dissolve the Mn_2O_3.

For the same type of mud, manganese drilling fluid, Elkatatny et al. 2012 [34] presented a new formulation containing 4% of glycolic acid. The designed formulation removed 75% weight of manganese tetraoxide (Mn_2O_3) drilling fluid filter cake. In this study, they reported that the solid liquid ratio used in the solubility test was (4 gm into 200 ml) at 190 °F. Increasing the concentration of the same acid to 5% weight removed 85 to 90% of filter cake formed by the same drilling fluid after 20 hours socking time. The filter cake removal stage with the glycolic acid was carried out after socking with an enzyme 10% weight for 24 hours. For the same removal condition, increasing the acid concentration up to 10% increased the removal efficiency up to 87%.

Recently, Al Moajil et al (2014) [35] presented a new formulation consisting of a combination of low HCl concentration (< 5 wt.%) and an organic acid such as lactic acid to remove the filter cake created by manganese tetraoxide water- based drilling fluids in one stage. The low concentration of HCl was safe to avoid releasing of chlorine gas, which is formed if high HCl concentration was used in the removal process.

2.2.2 Calcium Carbonate Filter Cake

Rostami A. and Nasr-El-Din H. (2010) [36] presented a new removal fluid to dissolve the filter cake formed by calcium carbonate weighted water based drilling fluid. Their formulation contained polylactic acid particles as removal for calcium carbonate filter cake. The removal efficiency reached up to more than 70% at 300 psi and 230 °F. Their removal method depended on self-destructing where the polylactic particles added to drilling fluid and it becomes a part of filter cake fabric after forming the filter cake. Then in next step where the filter cake contacted with water these particles hydrolyzed after enough time (20 hours) and produced lactic acid to dissolve the calcium carbonate filter cake solids.

Removal the filter cake formed by the formate drilling fluid that contained calcium carbonate, potassium formate and polymers (98 pcf, density) was studied by Al-Otaibi in 2008 [32]. The presented formulation was compatible with the formation brine so there was no participation formed in the permeable formation during the removal process. Using 10% weight of cellulose enzyme to break the polymeric coat around the filter cake solids and then an acetic acid 10% weight solution had better efficiency to remove the filter cake (more than 85%) and it was compatible with formation brine. Their test condition was 242 °F and 200 psi; the mixture was socked with filter cake for 17.5 hours.

2.3 Barite Solvent

This study focuses on developing a new formulation to remove the filter cake formed by barite weight water based drilling fluid. Such a formulation was not yet reported in the literature. In the subsequent paragraphs, a review of barium sulfate possible solvent that might be used in this study is presented.

Lakatos et al. [37][38] compared seven different barite solvents. Their work provided with the determination of the dissolution capacity of each solvent. The following chelating agent was presented in their study: Diethylenetriamine pentaacetic acid (DTPA), Ethylene-diaminetetraacetic acid (EDTA), hydroxyethyl ethylenediamine- triacetic acid (HEDTA), dioxaoctamethylene dinitrilo tetraacetic acid (DOCTA), nitrilotriacetic (NTA), (DCTA), and Triethylenetetramine hexaacetic Acid (TTHA). The chelating agents were prepared by the sodium base (NaOH). They conducted the experiments at 25°C which does not simulate the down hole conditions in oil and gas wells. Figure 2 summarized the result of different solvent capacity of barite in Kg of barite solids per cubic meter of solvent equivalent to gm of solids per litter of solvent (g/L). Based on the result of this study, DTPA performed the highest solubility of barite solids at 25 °C. Nevertheless, the barite particles solubility in the DTPA alone was about 8 g/L of 20% DTPA solution. Such solubility is only adequate to dissolve barite particles amount in about 0.4 mm thickness of filter cake in a well with 9 5/8 inches diameter whereas the filter cake thickness considered in most cases within the range of 1 to 3 mm used filed samples of barite weighted water base drilling fluid [3,4]. Therefore, there is a need for methods to dissolve the barite particles with capacity or a

need to enhance these types of chelating agent with using of some catalysts to improve the dissolution capacity.

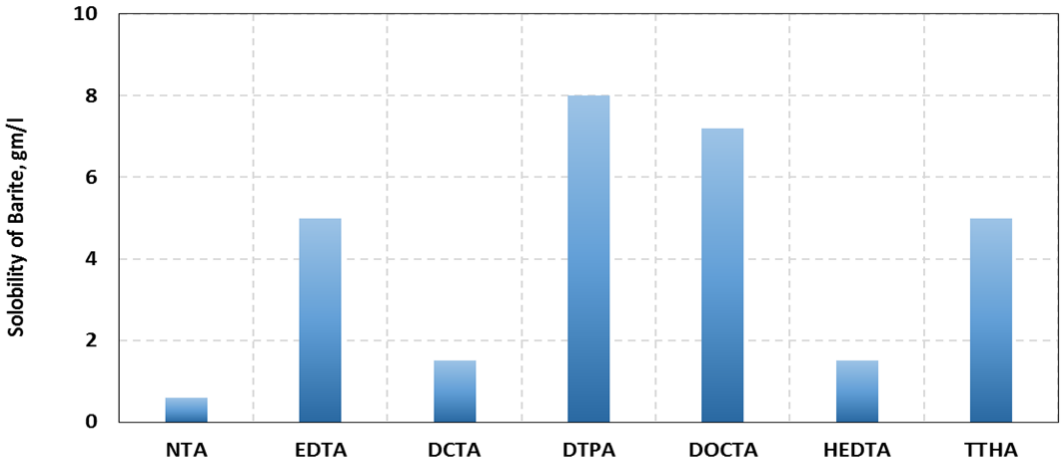


Figure 2 Barite Solvent at 25 °C [37]

Another study conducted by Putnis et al. [39] to investigate the dissolution rate of barite in DTPA at different concentrations and temperatures. The DTPA in their study was prepared by potassium base (KOH). The solubility test in their study was carried out using barite with particle size ranged (104–150μm) and the DTPA solution with concentration ranged (0.001M to 0.5M). The solubility test in this study was carried out with using of 1 gm of barite solids in 100 ml of DTPA solution. The results obtained by Putnis et al. [39] indicated that the lower concentration of DTPA achieved good dissolution rate at low temperature where the solubility of barite was found to be 1.17 g/L (650 ppm of Ba) in 0.05M DTPA solution in 19 hours at 22 °C. Increasing the temperature to 80°C showed that 0.5M of DTPA solution gave better results where 5280 ppm of barite dissolved in 0.5M DTPA and 4936 ppm dissolved in 0.05M.

Two barite dissolvers were evaluated using DTPA or ETDA as main solvent with to dissolve the barite scale by Nasr-El-Din et al. [40]. The solubility test was conducted to tests the two formulations and the results showed that the formulations of EDTA and DTPA yielded 23.7 g/L barite solubility. Although the results of these two formulations were effective but the composition was not disclosed. Thus in our study we will use the chelating agent and catalyst as one expected system to enhance the dissolution of barite solid particles in the chelating agents.

CHAPTER 3

RESEARCH OBJECTIVES AND METHODOLOGY

3.1 Statement of Problem

As reported in the literature, Barium Sulfate (Barite) is one of the widely used weighting materials in the preparation of drilling fluid for deep oil and gas wells. It is mostly preferred over other weighting materials due to its high density that provides adequate weight at low cost. However, dissolving barite has been a challenging problem, since the conventional solvents that utilize an oxidizer (e.g. persulfate), hydrochloric acid solution, organic (acetic, formic) acid, or a combination of acid and oxidizer are unsuccessful in dissolving barium sulfate. Barite, or barium sulfate, is insoluble in water or acid.

Several previous studies have been conducted on different types of filter cake removal formed by different types of drilling fluid such as calcium-carbonate- and manganese-filter cake. However, the removal of barite-containing filter cakes has been a challenging problem since the conventional filter cake removal treatments, although effective in removing calcium-carbonate- and manganese-containing filer cakes, are ineffective in dissolving barite-containing filter cakes. Therefore, an urgent need exists in the drilling and completion sector for a reliable fluid for degrading barite filter cake efficiently and completely.

Moreover, previous studies did not consider the wellbore constraints during their experiments and used chelating agent volume to barite weight ratio that cannot be

implemented in the real wells. In this study and for the first time we considered the wellbore volume, i.e., chelating agent volume that can be used, and the barite weight (filter cake) during the dissolution experiments. Although several attempts were conducted to increase the solubility of barite in chelating agents, there is still a need to examine different chelating agents in the presence of alkali and alkali earth hydroxides. Moreover, none of the previous studies added catalyst to the chelating agents to enhance the barite solubility. In this study, different chelating agents were used to enhance the knowledge of barite dissolution in different chelating agents prepared with different bases (KOH and NaOH) at high temperature.

3.2 Objectives

The main objective of this study is to address solution that is competent to remove the barite filter cake using chelating agents such as diethylenetriaminepentaacetic acid (DTPA), Ethylenediaminetetraacetic acid (EDTA) and (Hydroxyethyl) ethylenediaminetriacetic acid (HEDTA) in in the presence of different catalyst (converters). In order to achieve the main goal of this work the following sub-objectives were outlined:

(1) Use a high temperature solubility system to test and calibrate the optimal concentration of different chelating agents that can reach the maximal solubility of barite particles if using the chelating agent alone.

(2) Study the effect of different catalysts (converters) with various concentrations added to the obtained formulation in part (1) on the rate of barite dissolution. Study the dissolution rate as function of time and temperature.

(3) Investigate the compatibility between different enzymes and the formulation obtained in part (2) to determine the best enzyme. Also, the enzyme effect on barite dissolution will be investigated.

(4) Evaluate the filter cake removal efficiency formed by real field barite weighted water base drilling fluid samples using HPHT filtration test by using the designed formulation in part (3). Dissolution experiments such as those carried out in objective 1 will be repeated with the filter cake solids.

(5) Check the designed formulation efficiency by testing solubility rate of drilling fluid solids collected after separation process in the field.

(6) Study the microscopy and chemical structure of filter cake before and after the removal process using scanning electron microscopy SEM and X-ray Diffraction XRD.

(7) Understand the mechanisms of the barite reaction with the developed removal formulation and study the reaction kinetics of barite dissolution using surface area/pore size distribution, Fourier transform infrared spectroscopy (FTIR), and Rotating disk apparatus (RDA).

(8) Based on the experimental results, a dimensionless number will be developed that can predict the volume of the barite dissolver required to dissolve filter cake. This

number based on filter cake properties (e.g. thickness and mineral content) and the well geometry (open hole diameter and length).

3.3 Research Methodology

Solubility Test of Barite

The solubility experiments were carried out using 4 gm of barite in 100 ml of solvent. This ratio was obtained based on the ratio of barite solids weight to solvent volume as given in Equation (3.1). For a barite filter cake or scale formed around the wall of the well, the ratio of barite solids to the solvent is limited by the thickness of the formed cake, the diameter of the wellbore, and the porosity of filter cake [7]. The ratio of barite solids to the removal volume will be explained in detail in the next chapter.

$$W_R = \frac{d_h^2 - \left(d_h - 2th_f\right)^2 \times \rho_{fc}\ (1-\emptyset c)}{\left(d_h - 2th_f\right)^2} \qquad (3.1)$$

Where

dh : the diameter of the open hole section, cm,

Thf : the thickness of the filter cake, cm,

ρ_{fc} : the density of filter cake solids, g/cc, and

ϕc : the porosity of the filter cake, fraction.

The filter cake formed downhole should be very thin to avoid pipe sticking. A ratio of 4 gm/100 ml is used here to cover even the worst case of filter cake thickness reaching 1.5 mm [4] for open hole section with a hole size of 8 inches and above, Figure 3.

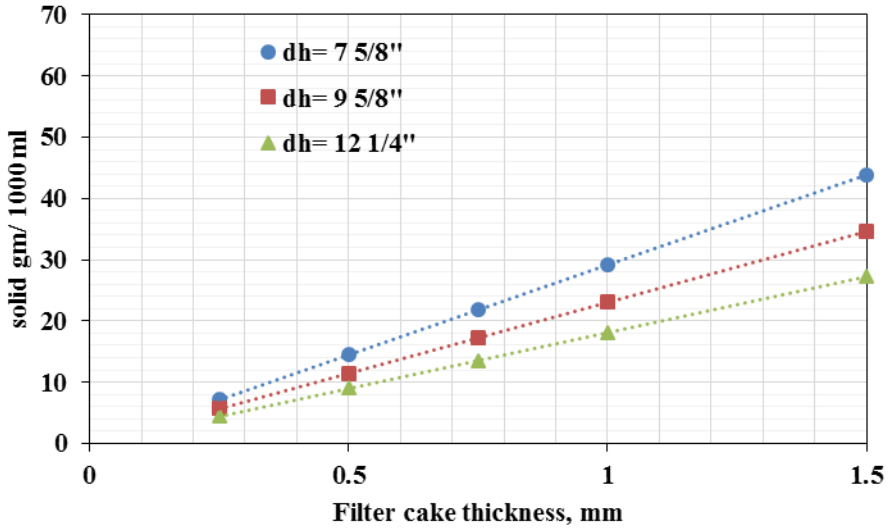


Figure 3 Recommended Solid-to-Liquid Ratio

The solubility experiments were conducted under constant stirring rate of 350 rpm. The solution was mixed using a flask connected to reflux condensers to ensure no water loss at high temperature, Figure 4. The following procedure was followed during the experiments:

a) 4 gms of the solids were mixed with 100 ml of the solvent (chelating agents).
b) The concentration of the chelating agents ranged between 10 wt% to 40 wt%. The experiments were carried out at 95°C (200°F) for a constant time of 24 hours and for a pH range between 11 and 12.
c) The dissolution rate of barite in the optimal type and concentration of chelating (obtained from steps (a and b) was studied as a function of time and pH. The pH was varied by preparing the powder chelating agent in different concentrations of NaOH and KOH solutions.
d) The weight of the barite at the beginning and the end of the experiment was measured. The solubility of the barite was measured using Equation (3.2).
e) Different catalysts such as potassium carbonate K_2CO_3, potassium chloride KCl, potassium formate $CHKO_2$, and others were added with diferent concentrations to determine the optimum catalyst type and concentration. The experiments were carried out at 95°C (200°F) for a constant duration of 24 hours.

$$solubility\% = \frac{dissolved\ barite\ weight}{initial\ barite\ weight} \times 100 \qquad (3.2)$$

Where: Initial barite weight is 4 gms in 100 ml of solvent; dissolved barite weight is the difference between the initial barite weight at start of the test and that taken at the end of the test.

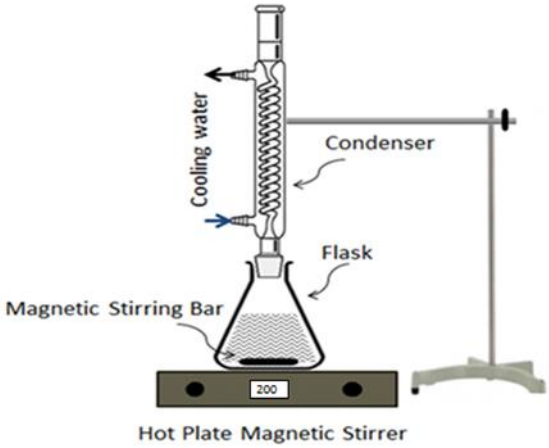


Figure 4 Solubility Test Setup at High Temperatures

Compatibility of Enzymes with Chelating Agents

Various enzymes were added to a given concentration of chelating agents from the solubility test to study their compatibily with chelating agents at 200°F. Two concentrations of the enzyme were used, viz., 7 wt. % and 10 wt. %. From solubility perspective, the dissolution rate of barite was measured in presence of a compatible enzyme in chelating agents.

Removal of Filter Cake Formed in HPHT

HPHT static fluid loss test was conducted at 300 psi differential pressure and at 270°F to form the filter cake using actual barite weighted water-based mud collected from the field. The filter cake was formed on ceramic disc using 500 ml cell. The filter cake removal treatment contained chelating agents with converting agent and one type of enzyme was used to study the filter cake removal efficiency. Two types of tests were used to evaluate the efficiency of the designed treatment solution. The first test was solubility test; the solubility of formed filter cake solids was measured by adding 4 gm of the filter cake solids to 100 ml of solution in Teflon cell. The Teflon cell placed in aging cell in hot rolling oven for 24 hours at 270°F and 300 psi. The second test was HPHT removal test. The formed filter cake was placed in HPHT cell with the removal fluid for 24 hour soaking time at 270°F and 300 psi differential pressure. The weight of filter cake before and after the removal process was recorded to determine the filter cake removal efficiency.

Solubility Test of Filter Cake Solids

The filter cake solids after filtration HPHT process are collected for its use in solubility test using the final formulation of the solvent. The collected filter cake solids are dried to

test the dissolution rate of dry solids of a filter cake. The test was conducted at different time intervals, viz., at 24, 48, 72, and 96 hours.

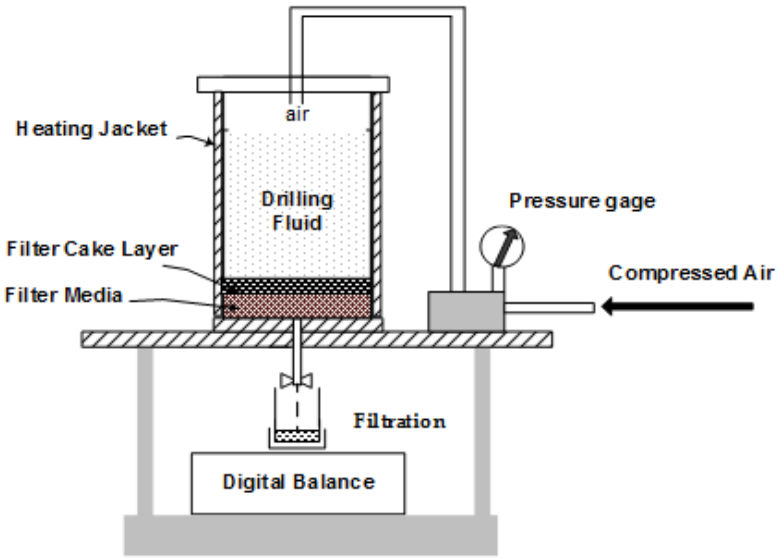


Figure 5 HPHT Filtration Cell, Forming Filter Cake

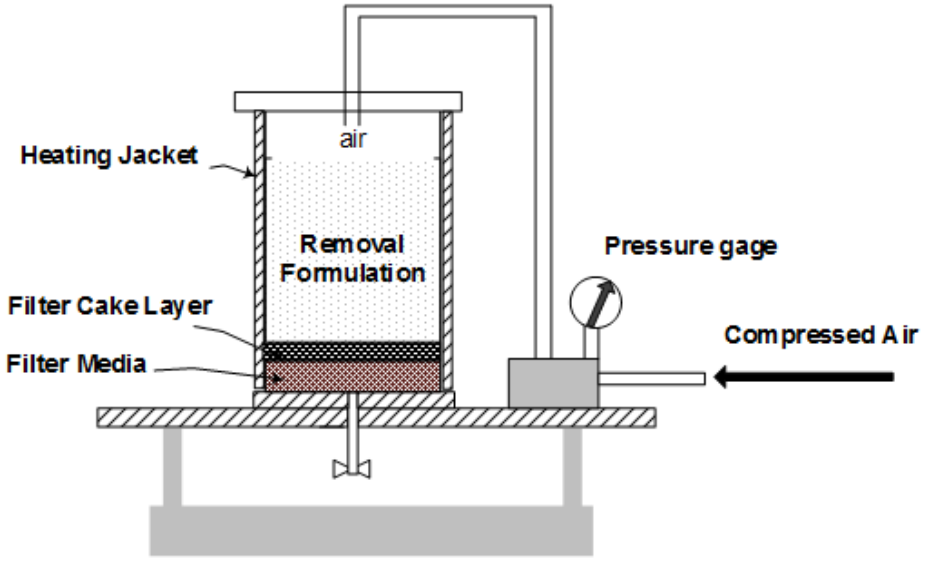


Figure 6 HPHT Filtration Cell, Filter Cake Removal Solubility

Rotating Disk Experiment

The barite solids will be prepared in a solid disk and then placed in the rotating disk apparatus to investigate the reaction kinetics of barite with the developed removal formulation at reservoir conditions.

Solids Analyses

The solids used in this study are dry industrial grade barite solids collected from de-sanders during well flow back and filter cake solids for actual water-based mud collected from drilling rig in Karan field. These solids are characterized using Scanning Electron Microscope (SEM). The SEM test was conducted to evaluate the composition of the solids before and after removal process. Further, the X-ray diffraction (XRD) is used to identify the mineralogy composition of the solids.

Figure 7 Rotating Disk Apparatus

Figure 8 Scanning Electron Microscope (SEM)

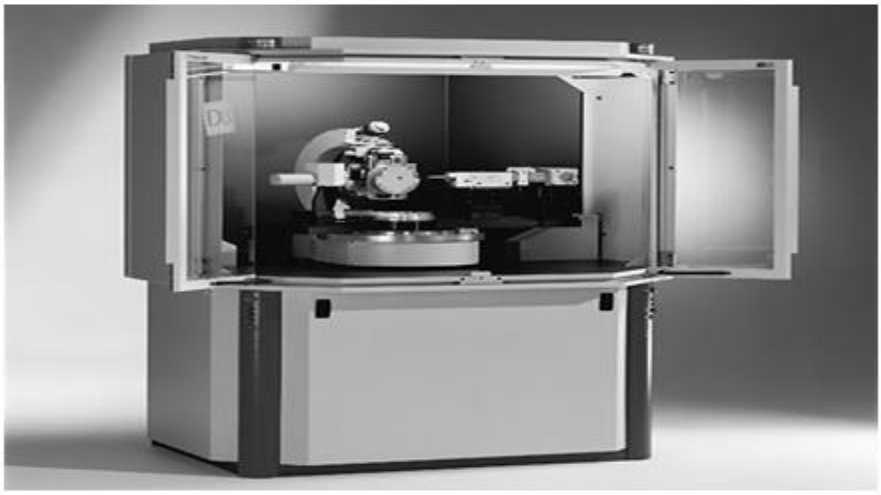


Figure 9 X-Ray Diffraction (XRD)

CHAPTER 4

FILTER CAKE PROPERTIES AND THEIR IMPACT ON REMOVAL

The main goal of this chapter is to consider the wellbore constraints and filter cake properties in the measurements of the chelating agent volume to barite weight ratio that can be implemented during the filter cake removal process in the real wells. Based on the results presented in this chapter, we considered the wellbore volume (chelating agent volume that can be used) and the barite weight (filter cake) during the dissolution experiments.

The filter cake evaluation involves many comprehensive testing and procedures to determine the filter cake properties such as thickness, mineralogy, porosity, permeability, and filtration to design the optimal mud program. For the maximum reservoir contact (MRC) and extended reach (ER) wells where the horizontal section could be 3000 ft or more in those wells, the filter cake formed by the drilling fluid varied from one section to another in the long horizontal section. Therefore, the process of filter cake removal in maximum reservoir contact and extended reach wells should consider the variation in the filter cake properties to achieve an efficient removal process.

This chapter focuses on evaluating the filter cake thickness, porosity and permeability profile through the horizontal wells. Moreover, the impact of the filter cake porosity and thickness on the removal process is presented in this work. To achieve the objective of this work, high pressure high temperature (HPHT) fluid loss test was conducted to form the

filter cake using actual drilling fluid samples. The compositional and structural analysis of filter cake was carried out using scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-Ray Fluorescence (XRF). The drilling fluid studied samples were collected from real field rig while drilling the horizontal section.

The results showed that the maximum thickness of the filter cake was 1.3 mm. The drilling operation was initiated with drilling fluid that was capable of forming a filter cake with low porosity (5%) and permeability (0.01 md) to minimize the filtration volume. In the first part of the horizontal section the filter cake porosity and permeability increased sharply as more feet of horizontal section drilled. The porosity increased to about 35% and permeability to 0.25 md. After that it remains stable with slight decrease. This growth in the filter cake porosity from 5 to 35% reduced the liquid to solid ratio in the removal process from 28 gm per 500 ml up to 18 gm per ml.

The result of this work linked the filter cake properties (thickness, porosity, and mineralogy) in the maximum reservoir contact and extended reach wells with Solids-to-Liquid Ratio needed to be used in the filter cake removal process. This work will help to reevaluate the filter cake removal and stimulation recipes that were designed based on constant filter cake properties.

4.1 Experimental Studies

4.1.1 Materials

The drilling fluid samples used in this study were collected from horizontal well in an oil field during the drilling of the horizontal section. The drilling fluid sample was collected from flow line immediately after the shale shaker with the beginning of drilling the horizontal section.

4.1.2 Experimental Procedure

High Pressure Static Filtration Tests

Static loss test was conducted at 300 psi differential pressure and 25˚C. The inlet pressure was 500 psi and the back pressure was 200 psi. The tests were performed using 500 ml HPHT cell. The ceramic disks (35 micron) were used as filtration medium in the test to match the properties of sandstone formation. The disk diameter was 2.5 inch and the thickness was 0.25 inch.

Filter Cake Thickness

After the static filtration test was run, the excess drilling fluid was decanted and the filter cake was carefully removed from the API cell and then washed gently. The filter cake thickness was measured by the direct method by using Vernier caliper or ruler after removing the filter cake from the fluid loss cell.

Filter Cake Porosity

Dewan and Chenevert [28] presented a method to measure filter cake porosity. They used the basic fundamental definition of porosity (e.g. the porosity equal to the pore volume divided by bulk volume$\emptyset = V_p/V_b$) to determine the porosity of the cake. Where the pore volume is equal to the fluid volume and the bulk volume is equal to the solids volume of the cake plus the total pore volume of the cake.

The porosity of the filter cake was determined by removing the filter cake from the filtration cell and taking the wet or initial weight (filter cake plus the filtrate paper). The wet weight of paper and filter cake combination (as 100% saturated with filtrate) is measured with highly sensitive balance of 0.01 gm resolution balance. The weight of the wet paper is subtracted to get the net wet weight of the filter cake. Then the cake is dried at 100˚C for 24 hours to dry the water (in water base mud) and its dry weight is measured, and then the weight of the dry filtrate paper is subtracted to give a net dry weight of the filter cake. Denoting the fluid and grain densities by ρ_f and ρ_g respectively, the porosity of the cake $\emptyset_c$ can be calculated as follows:

$$\emptyset_c = \frac{\propto}{\propto + \frac{\rho_f}{\rho_g}} \qquad (4.1)$$

Where:

$$\propto = \frac{\text{net wet weight of the cake}}{\text{net dry weight of the cake}} - 1 \qquad (4.2)$$

The bulk volume of the filter cake can be calculated by using the value of the filter cake thickness and the internal diameter of the fluid loss cell.

4.2 Results and Discussion

The filter cake formed by the collected drilling fluid samples during the drilling operation shows that the drilling fluid was designed to form good sealing filter cake as shown in Figures 10. The characterization results using SEM, XRF and XRD showed that there is a percentage of the formation minerals in the filter cake solids ranged from 10 to 40 wt.%. However, the sharp increment in the filter cake porosity and permeability is not only caused by the formation cuttings content. The reason of this sharp increment in the first part of the horizontal section because of the un-uniformed shape of the formation drilled-cuttings circulated with the drilling fluid. Continuous circulation of these solids make it very fine and break the un-uniformed shape which illustrates the stability of the filter cake porosity values in the last part of the horizontal well, as shown in Figure 10.

From the removal point of view, the first stage to come up with chemical filter cake removal treatment is to test the solubility of the filter cake solids in the designed solution. The ratio of the filter cake solids to the liquid volume of the filter cake removal volume was not discussed as function of the filter cake properties. In the next section detailed discussion about how to calculate the filter cake solid to solvent volume ratio based on the filter cake properties parameters such as filter cake thickness, filter cake porosity, and density of the filter cake solids will be provided. The well geometry parameters such as the open hole diameter and the length of the treated section were also included in the removal ratio of filter cake to solvent volume.

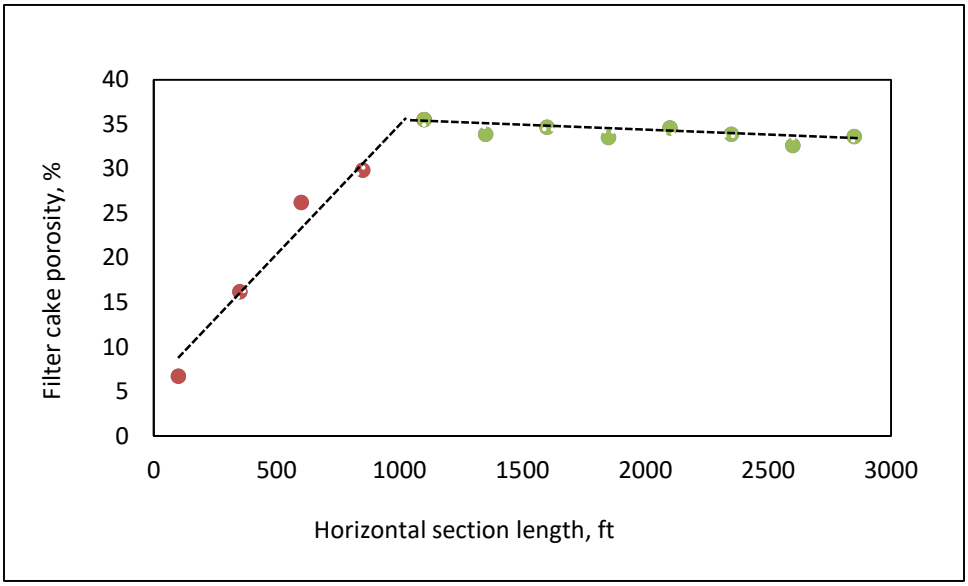


Figure 10 Filter cake porosity profile along the horizontal section of the well

4.3 Removal Process

4.3.1 Solid to Volume of Liquid Ratio:

In this section, we will provide the calculation of the volume of the solution required to remove the filter cake solids based on material balance calculations as shown in Figure 11. The volume of filter cake (V_{fc}) in certain length of the well can be given as follows:

$$V_{fc} = \frac{\pi}{4} L \left[\left(d_h^2 - \left(d_h - 2th_f\right)^2\right]\right. \quad (4.3)$$

Where:

V_{fc} = the volume of filter cake

L = the length of the hole

d_h = the diameter of the open hole

t_{hf} = the thickness of the filter cake.

The weight of filter cake solids in the calculated V_{fc} volume can be calculated as follows:

$$W_{fc} = V_{fc} \times \rho_{fc} \quad (4.4)$$

Where:

ρ_{fc} = density of filter cake solids

W_{fc} = weight of filter cake solids.

Equation (4.4) calculated the weight of the filter cake assuming that there is no porous (filter cake porosity = zero). The volume of the open hole (or the solvent) (**V_{fl}**) can be calculated as follows:

$$V_{fl} = \frac{\pi}{4} L \left(d_h - 2th_f\right)^2 \quad (4.5)$$

The ratio of the two volumes (V_R) can be simplified to:

$$V_R = \frac{d_h^2 - \left(d_h - 2th_f\right)^2}{\left(d_h - 2th_f\right)^2} \quad (4.5)$$

Since filter cake solids have a specific gravity ranged from 2 to 4 depends on weighting material used in the drilling fluid (e.g. barite, calcium carbonate, and hematite and others); the weight to volume ratio (W_R) can be given by:

$$W_R = \frac{\left[d_h^2 - \left(d_h - 2th_f\right)^2\right] \times \rho_{fc}}{\left(d_h - 2th_f\right)^2} \quad (4.6)$$

The unites of the open hole diameter and filter cake thickness have to be the same (e.g. inch). The unit of Solids-to-Liquid Ratio depends on the density unit for instance gm/ml.

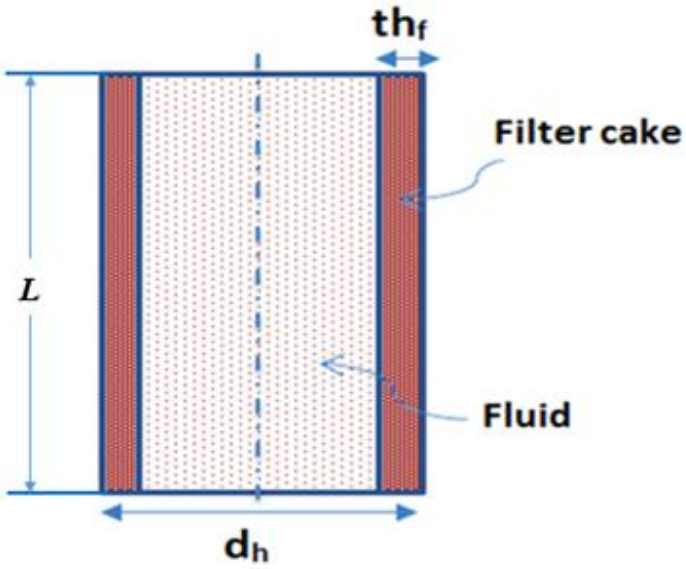


Figure 11 Representation of the Filter Cake on the Wall of the Formation

4.3.2 Effect of Filter Cake Density on Solids-to-Liquid Ratio:

For a gas well with 9 5/8 inch hole diameter and a filter cake thickness of 2 mm, this ratio as function of the filter cake density is shown in Figure 12. In case of filter cake solids density equals to 3.5 the Solids-to-Liquid Ratio is (20 gm of solids per 1000 ml). The solid/liquid ratio in the well is a function of the filter cake thickness and well diameter if we assume that constant average of filter cake density through the whole horizontal section. Figure 12 shows the relationship between the filter cake thickness and solid/ liquid ratio in (gm solids/ 1000 ml of solvent). Figure 12 presents the effect of filter cake density on the solid/ liquid ratio for constant well diameter 9 5/8 inch. Figure 12 was generated assuming filter cake porosity zero as worst case.

The effect of the filter cake solids density becomes significant on the solid/ liquid ratio as the filter cake thickness increases. For instant, when the filter cake thickness equals to 1mm the solid/ liquid ratio increased by 13 gm from 13 to 26 gm/1000 ml as the filter cake solids density decreased by 2 g/cc from 4 to 2 g/cc as shown in Figure 12 and 13.

Meanwhile, the the solid/ liquid ratio increased by 25 gm from 27 to 52 gm/1000 ml as the filter cake solids density decreased by 2 g/cc from 4 to 2 g/cc for the filter cake thickness 2mm as shown in Figure 13. The previous analysis was developed on the basis of zero filter cake porosity as worst case.

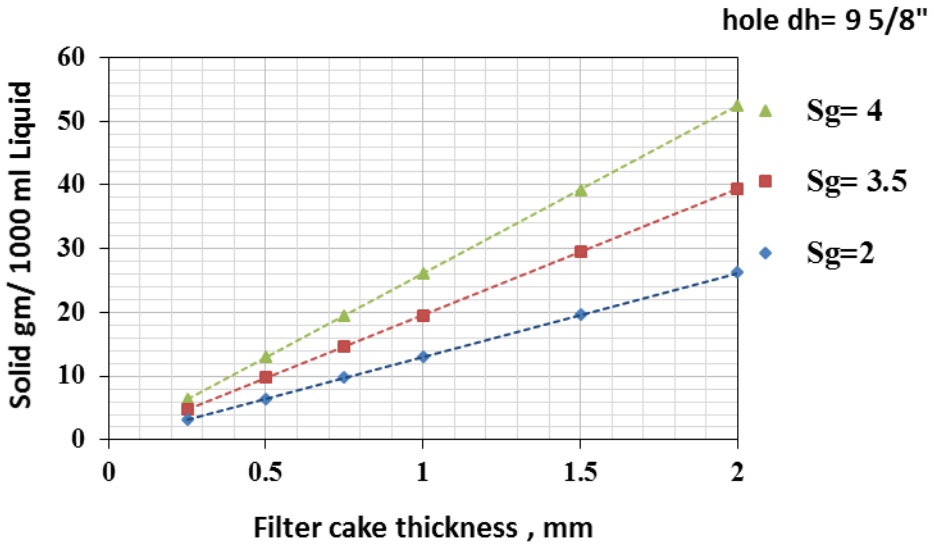


Figure 12 Filter Cake Solids Weight to Removal Volume Ratio*

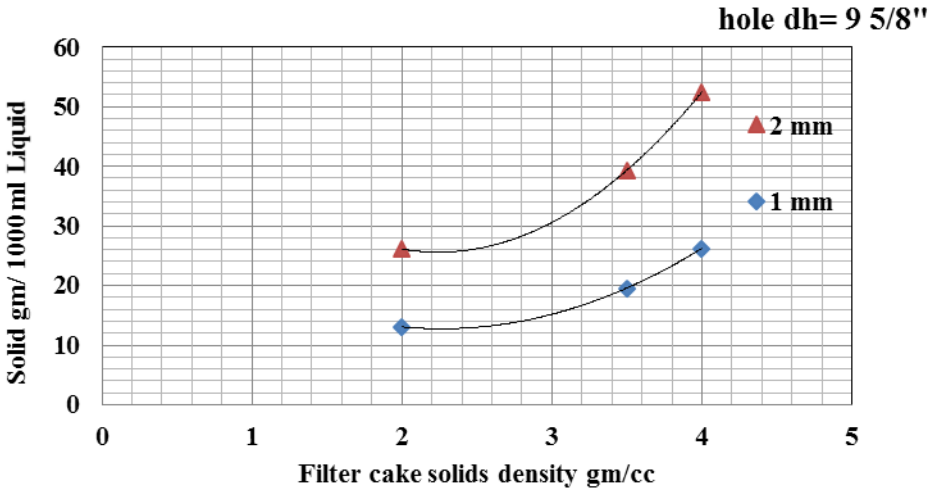


Figure 13 Effect of Filter Cake Density on Solids-to-Liquid Ratio*

**Filter cake solids to removal volume ratio as function filter cake thickness for different filter cake solids density at constant open hole diameter (9 5/8 inches) (zero filer cake porosity).*

4.3.3 Effect of Filter Cake Porosity on Solids-to-Liquid Ratio:

As mention before the filter cake in the Solids-to-Liquid Ratio equation's (4.6) are calculated assuming that the filter cake porosity is zero. As the results obtained by this study; the porosity of the filter cake in the horizontal section increased in the first part and reached up to and average value of 0.35. Therefore, adding the porosity term to equation (4.6) the filter cake solids weight to volume ratio will be given by:

$$W_R = \frac{d_h^2 - \left(d_h - 2th_f\right)^2 \times \rho_{fc}\ (1-\emptyset c)}{\left(d_h - 2th_f\right)^2} \qquad (4.7)$$

Where: ϕc = filter cake porosity

The same analysis were re-evaluated taking into account the porosity of cake equal to 35% as an average value for the porosity of the filter cake in the horizontal section. The result is shown in Figure 14. It is very clear that the solid/ liquid ratio decreased for the case of filter cake porosity equals 35%. For example, there is about 19 gm/1000 ml decline in the solid/ liquid ratio from 52 to 33 gm/ 1000 ml by considering the porosity value of filter cake (35%) assuming that the filter cake thickness is 2 mm and the filter cake solids density 4 g/cc as shown in Figure 14. The drop in the Solids-to-Liquid Ratio caused by condensing the filter cake porosity becomes minimal in case of low density of the filter cake solids or in case of small thickness.

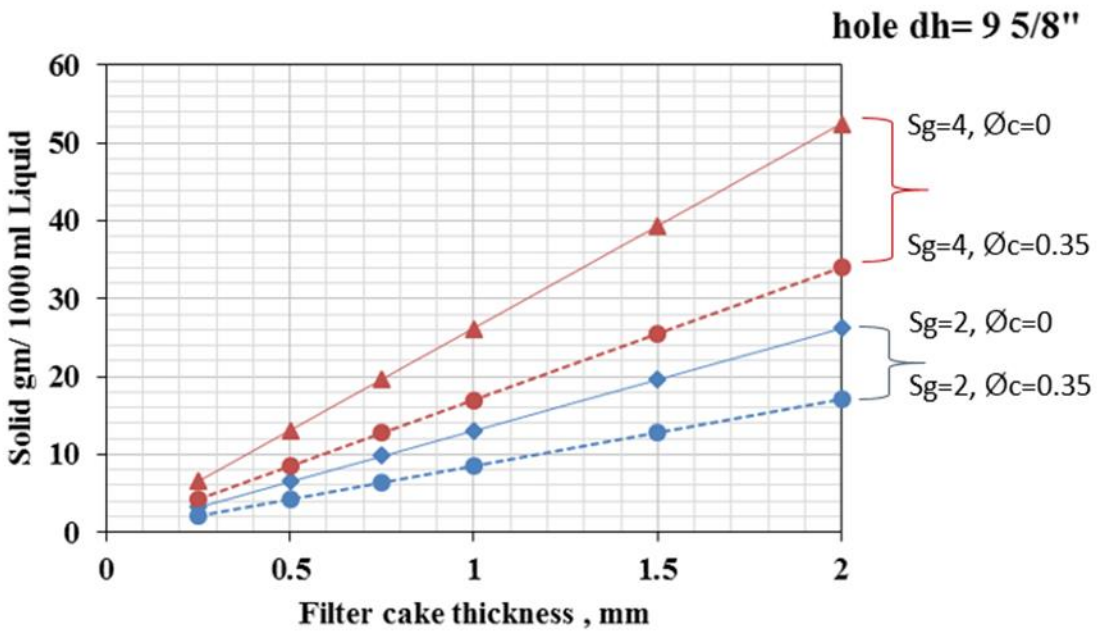


Figure 14 Effect of Filter Cake Porosity on Solids-to-Liquid Ratio

4.3.4 Effect of Hole Diameter on Solids-to-Liquid Ratio:

The relationship between the filter cake thickness and solid/liquid ratio in the removal process as function of different open hole diameter for constant density of the filter cake solids is shown in Figure 15. It is clearly that for a constant filter cake thickness the solid-to-liquid ratio decreases with increasing the open hole diameter.

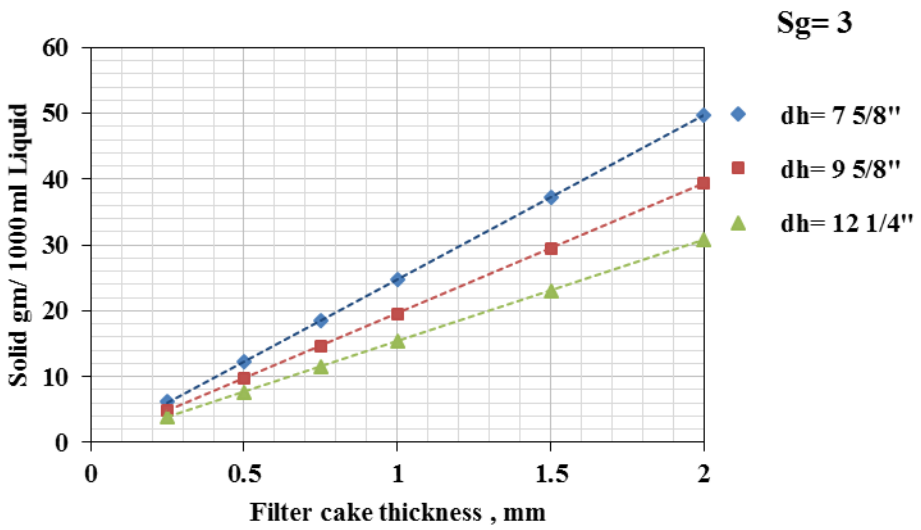


Figure 15 Effect of Hole Diameter on Solids-to-Liquid Ratio

4.4 Summary

In this study drilling fluid samples were collected from different location during drilling the horizontal section of maximum reservoir contact and extended reach wells to evaluate the filter cake properties through the horizontal section of the well. The impact of the change in the filter cake properties on the filter cake removal design from Solids-to-Liquid Ratio point of view was investigated. The following are the conclusions that were drawn from this study:

- The initial filter cake porosity was (5%) and permeability (0.01 md) at the beginning of the drilling operation.
- Along the horizontal section, in the first part of the horizontal section the filter cake porosity increased sharply as more feet of horizontal section drilled. The porosity increased to about 35%. After that it remains stable with slight decrease.
- For the case assumed in this study of (open hole diameter equals to 9 5/8 inches and filter cake thickness of 2 mm); considering the average filter cake porosity as 35%, as obtained in the result of work, the ratio of the treatment liquid volume needed in the filter cake removal to the filter cake solids reduced from 52 to 33 gm/ 1000 ml.
- Based on our results, the recommended value of filter cake solids to solvent ratio to be used in future work for testing the filter cake removal is to use 4 gm of filter cake solids in 100 ml of solvent. This recommended ratio almost represent of an average 2 mm filter cake thickness and open hole diameter around 9 5/8

inches. The ratio can be re adjusted if one of the following parameters filter cake thickness, porosity and open hole diameter change.

- Up scaling the reduction of the Solids-to-Liquid Ratio with considering the porosity value of the filter cake leads to reduction in the removal process cost.

CHAPTER 5

EVALUATION OF BARITE SOLUBILITY USING DIFFERENT CHELATING AGENTS

As mention previously, Barium Sulfate (Barite) is not soluble in the regular solvents such as hydrochloric acid (HCl) and other acids. Therefore, in this chapter we focused on evaluating the dissolution of the industrial barite particles in different chelating agents. Chelating agents such as; Diethylenetriaminepentaacetic acid (DTPA), Ethylenediamine-tetraacetic acid (EDTA), and Hydroxyethylethylenediaminetriacetic acid (HEDTA) with high and low pH were used in this study.

The effect of the base of chelating agents, alkali and alkali earth hydroxides, on the dissolution of barite was investigated. For the first time, the optimum pH, concentration, and base (sodium or potassium) of chelating agents that yielded the maximum dissolution were investigated in this study at high temperature. Previous studies did not consider the wellbore constraints during their experiments and they used chelating agent volume to barite weight ratio that cannot be implemented in the real wells. In this study and for the first time we considered the wellbore volume (chelating agent volume that can be used) and the barite weight (filter cake) during the dissolution experiments.

Based on the results obtained from this study, potassium base DTPA-K_5 and EDTA-K_4 of 20wt% concentration were found to be the most effective chelating agents to dissolve barite. The solubility of barite was found to be 26.8g/L in solution containing 20wt% of

DTPA-K_5 and 25.6g/L in solution containing 20wt% of EDTA-K_4 in 24 hours soaking time and pH above 11 at 200°F.

5.1 Introduction

Barium Sulfate (Barite) is one of the common weighting materials used in drilling fluid for deep oil and gas wells. It is mostly preferred over other weighting materials such as iron oxides, calcium carbonate, and others due to its high density that provides adequate weight at low cost [41]. Consequently, the main source of formation damage during drilling is the weighting material used in drilling fluids [3]. Due to the wide use of barite in field applications, there is a need for deep understanding of the barite dissolvers at field conditions to formulate a treatment that can dissolve the barite solids that are formed during drilling or production operations. The low solubility of barium sulfate in water (2.3 mg/L) leads to the formation of barium sulfate scale in oil and gas wells [42]. On the other hand, contacting the high sulfate seawater with barium in the underground formations is another source of the barite scale precipitation [43,44].

The solubility of Barite in chelating agents was investigated but the optimum conditions for dissolution were not completely addressed. Lakatos et al. [37,38] compared seven different barite dissolvers. Their work provided with the determination of the dissolution capacity of each solvent. The following chelating agents were used in their study; Diethylenetriaminepentaacetic acid (DTPA), Ethylene1diaminetetraacetic acid (EDTA), hydroxyl-ethylethylenediaminetriacetic acid (HEDTA), dioxaoctamethylenedinitrilote-traacetic acid (DOCTA), nitrilotriacetic (NTA), (DCTA), and Triethylenetetramine-

hexaacetic Acid (TTHA). They conducted the experiments at 25°C which does not simulate the down hole conditions in oil and gas wells. Their results showed that the barite particles solubility in the DTPA was about (8 g/L) in a solution containing 0.1 mole/litter concentration DTPA. The chelating agents were prepared by the sodium base (NaOH) in Lakatos' study [37]. Another study conducted by Putnis et al. [39,45] to investigate the dissolution rate of barite in DTPA at different concentrations and temperatures. The DTPA in their study was prepared by potassium base (KOH). The solubility test in their study was carried out using barite with particle size ranged (104 -150 μm) and the DTPA solution with concentration ranged (0.001M to 0.5M). The particle size of the barite they used in their experiments is completely different than the one used in oil and gas wells drilling fluid. In this study we used industrial grade barite that is typically used in drilling fluid for deep oil and gas wells.

The results obtained by Putnis et al. [39] indicated that the lower concentration of DTPA achieved good dissolution rate at low temperature where the solubility of barite was found to be 1.17 g/L (650 ppm of Ba) in 0.05M DTPA solution in 19 hours at 22 °C. Increasing the temperature to 80°C showed that 0.5M of DTPA solution gave better results where 5280 ppm of barite dissolved in 0.5M DTPA and 4936 ppm dissolved in 0.05M.

Two barite dissolvers were evaluated using DTPA or ETDA as main solvent to dissolve the barite scale by Nasr-El-Din et al. [40]. The solubility test was conducted to test the two formulations and the results showed that the EDTA and DTPA yielded 23.7 g/L barite solubility. Although the results of the two formulations were effective but the composition was not disclosed.

Several attempts were conducted to increase the solubility of barite in chelating agents, but still there is a need to examine different chelating agents in the presence of alkali and alkali earth hydroxides. In this study, different chelating agents were used to enhance the knowledge of barite dissolution in different chelating agents prepared with different bases (KOH and NaOH) at high temperature (200°F). The current study objectives are to; (1) evaluate the barite dissolution rate using different chelating agents with different bases (sodium base (NaOH) or potassium base (KOH), (2) present the right approach to prepare the chelating agent to get the maximum dissolution rate of barite, (3) evaluate the optimum dissolution time, (4) study the effect of the pH on barite dissolution, and (5) understand the mechanism behind the barite dissolution by chelating agents using FTIR (Fourier Transformation Infra-Red) and SEM (Scanning Electron Microscope). The results of this work will help formulate a treating formulation for cleaning the barite scale from surface and subsurface facilities and cleaning the wellbore after drilling operations of deep oil and gas wells drilled using barite-based mud.

5.2 Materials and Experimental Work

5.2.1 Materials

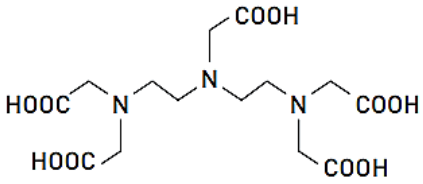
Industrial barite (barium sulfate) grade was used to carry out the experimental work of this study. The barite particles were sieved using 75 micron mesh size to insure the same particle size range of barite (less than 75 Mic) is used in all experimental.

Eight chelating agents were used in this study; diethylenetriaminepentaacetic acid (DTPA) potassium salt and sodium salt base, ethylenediaminetetraaceticacid (EDTA) potassium salt and sodium salt base, hydroxyethylethylenediaminetriacetic (HEDTA) acid sodium salt and glutamicdiacetic acid (GLDA) sodium salt.

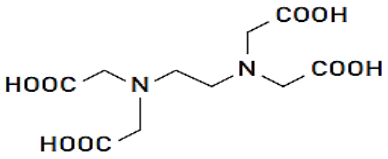
The molecular structure shows that each chelating agent has a certain number of carboxylate functional groups (ligands) which bind to metal centre having different number of nitrogen atoms [39,46]. For example DTPA has five ligands linked with three nitrogen atoms in the centre. At high pH the ligand forms strong 1:1 chelates in solution [46]. Based on that the ligand can be either Na or K based on the used base to prepare the solution; in our study NaOH and KOH were used to prepare the solution.

Table 1 Chelating Agents Used in this Study

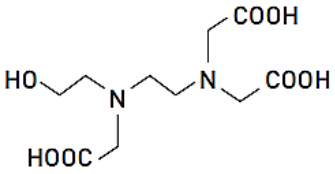
Chelating Agents		**Appearance/ Form/ Assay**	**Chemical Formulation**
1	DTPA	99% Powder	$C_{14}H_{23}N_3O_{10}$
2	DTPA – Pentasodium (DTPA-Na_5)	40% aqueous solution	$C_{14}H_{18}N_3\ Na_5O_{10}.5H_2O$
3	DTPA – Pentapotassium (DTPA-K_5)	40% aqueous solution	$C_{14}H_{18}N_3\ K_5O_{10}.5H_2O$
4	EDTA	98-100% Powder	$C_{10}H_{16}N_2O_8$
5	EDTA – Di Sodium (EDTA-Na_2)	98-100% Powder	$C_{10}H_{14}N_2Na_2O_8.2H_2O$
6	EDTA – Di Potassium (EDTA-K_2)	99% Powder	$C_{10}H_{14}N_2K_2O_8.2H_2O$
7	EDTA – Tetra Sodium (EDTA-Na_4)	39% aqueous solution	$C_{10}H_{12}N_2Na_4O_8.4H_2O$
8	EDTA – Tetra Potassium (EDTA-K_4)	39% aqueous solution	$C_{10}H_{12}N_2K_4O_8.4H_2O$
9	HEDTA – Tri Sodium (HEDTA-Na_3)	40% aqueous solution	$C_{10}H_{15}N_2Na_3O_7.3H_2O$
10	GLDA – Tetra Sodium (GLDA-Na_4)	38% aqueous solution	$C_9H_9NNa_4O_8.4H_2O$



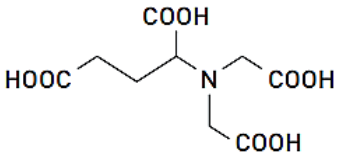
Diethylenetriaminepentaacetic acid
DTPA-H_5



Ethylenediaminetetraacetic acid
EDTA-H_4



Hydroxyethylethylenediaminetriacetic acid
HEDTA-H_3



Glutamic acid, N,N-diacetic acid
GLDA-H_4

Figure 16 Molecular Structure of the chelating agents [45,46]

*The structure of the DTPA-K_5/ $Na_5$is same as DTPA with replacing the H_5 with K_5, similarly for others.

5.2.2 Experimental Work

The solubility experiments were carried out using 4 gm of barite in 100 ml of solvent. This ratio was obtained based on the ratio of barite solids weight to solvent volume as given in Equation (5.1). For a barite filter cake or scale formed around the wall of the well, the ratio of barite solids to the solvent is limited by the thickness of the formed cake and the diameter of the wellbore as well as the porosity of filter cake [7].

$$W_R = \frac{d_h^2 - \left(d_h - 2th_f\right)^2 \times \rho_{fc}\ (1-\emptyset c)}{\left(d_h - 2th_f\right)^2} \qquad (5.1)$$

Where

d_h : the diameter of the open hole section, cm,

T_{hf} : the thickness of the filter cake, cm,

ρ_{fc} : the density of filter cake solids, g/cc, and

ϕ_c : the porosity of the filter cake, fraction.

Although the filter cake formed downhole should be very thin to avoid pipe sticking, using a ratio of 4 gm/100 ml covers even the worst case of filter cake thickness that reached 1.5 mm [4] for open hole section with hole size of 8 inches and above, Figure 17.

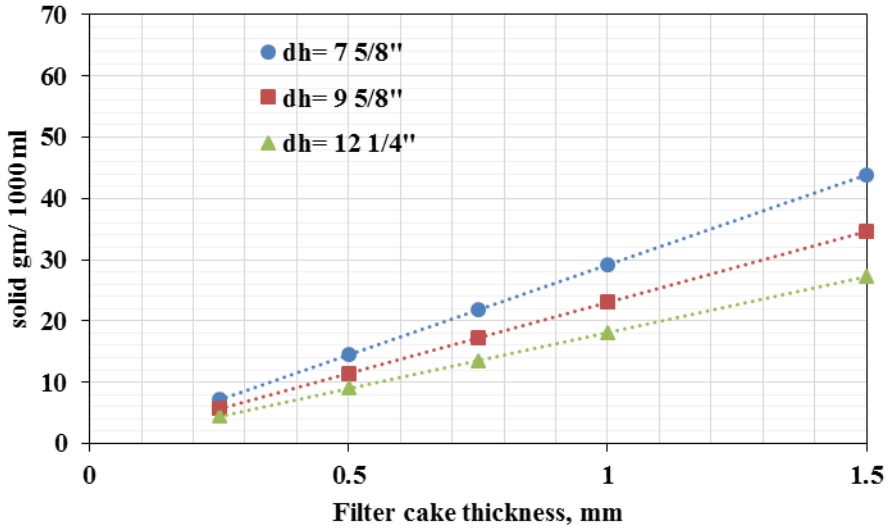


Figure 17 Recommended solid-to-liquid ratio based on filter cake thickness and hole size

The solubility experiments were conducted under constant stirring rate (350 rpm) and the solution was mixed using flask connected to reflux condensers to ensure no water loss at high temperature, Figure 18. The following procedure was followed during the experiments:

a) Mixing 4 gm of the industrial barite with 100 ml of chelating agent (1) for example DTPA-Na_5. The concentration of the chelating agents ranged between 10 wt% to 40 wt%. The experiments carried out at 95°C (200°F) for constant time (24 hours) and at high pH ranged (11 – 12).
b) Repeat step (a) using different chelating agents (DTPA-Na_5, DTPA-K_5), (EDTA-Na_2, EDTA-Na_4, EDTA-K_2, EDTA-K_4,), (GLDA-Na_4) and (HEDTA-Na_3) with different concentrations.
c) The dissolution rate of barite in the optimal type and concentration of chelating (obtained from steps (a and b) was studied as function of time and pH. The pH was varied by preparing the powder chelating agent in different concentrations of NaOH and KOH solutions.
d) The weight of the barite at the begging and the end of the experiment was measured. The solubility of the barite was measured using the following equation:

$$solubility\% = \frac{dissolved\ barite\ weight}{initial\ barite\ weight} \times 100 \qquad (5.2)$$

Where: Initial barite weight is 4 gm in 100 ml of solvent; dissolved barite weight is the difference between the initial barite (start of the test) and remaining barite (at the end of the test).

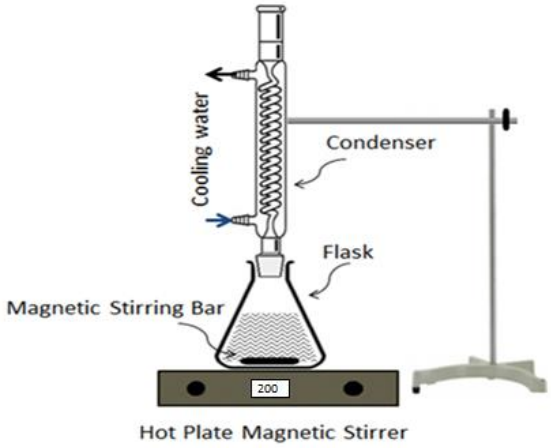


Figure 18 Assembled Solubility Test Setup at High Temperatures

5.3 Characterization and Analysis

Scanning Electron Microscope (SEM)

The chemical composition of the industrial barite was determined using Scanning Electron Microscope (SEM-EDS) to evaluate the purity of barite before the dissolution with the chelating agent. Similarly, the composition of the solids remaining after the dissolution was evaluated to study the change of the chemical composition during the solubility test. The surface area structure of the barite was estimated according the high resolution SEM pictures before and after the dissolution with chelating agent. The samples were dried for at least 6 hours and then gold-coated to be viewed using the SEM's specimens.

X-Ray Diffraction Analysis

X-ray diffraction spectroscopy was used to measure the mineralogy of the industrial barite (using with PANalytical X-ray, Philips Analytical). The XRD data was used as a confirmation for the EDS analysis results. The XRD also was carried out to determine the mineralogy of the solids precipitated at the end of the solubility test.

Fourier Transform Infrared Spectroscopy (FTIR)

The surface functional groups of industrial barite before and after the dissolution were evaluated using Fourier transform infrared (FPC FTIR Perkin Elmer spectrophotometer) analysis. A pellet was prepared by mixing (1- 2 mg) of the barite with 100 mg of KBr. Then the sample was exposed to a laser beam in the FTIR instrument. The instrument wave number ranges from 4000 to 400cm^{-1}.

Particle Size Analysis

The particle size distribution of the industrial barite solids was measured using the Wet Dispersion Unit ANALYSETTE 22 Nano Tec plus.

5.4 Results and Discussion

5.4.1 Solubility of Barite in DTPA

As shown in Table 1, the Diethylenetriaminepenta acetic (DTPA) acid is available in powder form (99% Mw 393.4) and as aqueous solution of 40wt% concentration. The DTPA solution exists either as potassium base or sodium base, viz., Diethylenetriaminepentapotassium (DTPA-K_5) and pentasodium acetic acid (DTPA-Na_5), respectively. The DTPA solution was prepared as aqueous solution using either NaOH [37] or KOH [39][45]. The hydroxide compounds were used to increase the pH of the distilled water. Since the chelating agent (DTPA-H_5 powder) solubility in the distilled water is limited, the pH of the water must be raised to prepare the aqueous solution. Increasing the pH of the water either by using the NaOH or KOH increased the chelating agent solubility.

The DTPA solution potassium base was tested at variable concentrations ranging from 10 to 40 wt%. These concentrations were prepared by diluting the 40 wt % DTPA-K_5. The pH of the DTPA was kept in the range of 11- 12. The dissolution capacity of the Barite in DTPA potassium base is shown in Figure 19. The results show that the 20 wt% concentration of DTPA-K_5 at high pH (11 - 12) yielded the maximum dissolution rate of

barite particles. The test was run for 24 hours at 200 °F. The maximum removal capacity was about 67 wt% (equal to 26.8 grams of industrial barite per liter of 20 wt% DTPA-K_5), as shown in Figure 19 and 20.

Sodium hydroxide was used to increase the pH to 12 to prepare the sodium base of the DTPA-Na_5. The same experimental conditions of 200 °F and 4 gm of barite in 100 ml of solvent were applied for this purpose. Various concentrations of DTPA-Na_5 were prepared to optimize the concentration of DTPA-Na_5. The pH of the solution was kept in the range of 11 to 12. The experimental results show that about 15 gm of barite particles was dissolved (38 wt% solubility percentage) at the 20 wt% optimum concentration of DTPA as shown in Figure 19 and 20.

The potassium base of the DTPA chelating agent (DTPA-K_5) yielded higher dissolution rate of barite compared to the sodium base, Figure 19. Therefore special attention was given here to study the effect of pH on the dissolution of barite in 20 wt% DTPA-K_5 (optimum concentration as shown in Figure 19).

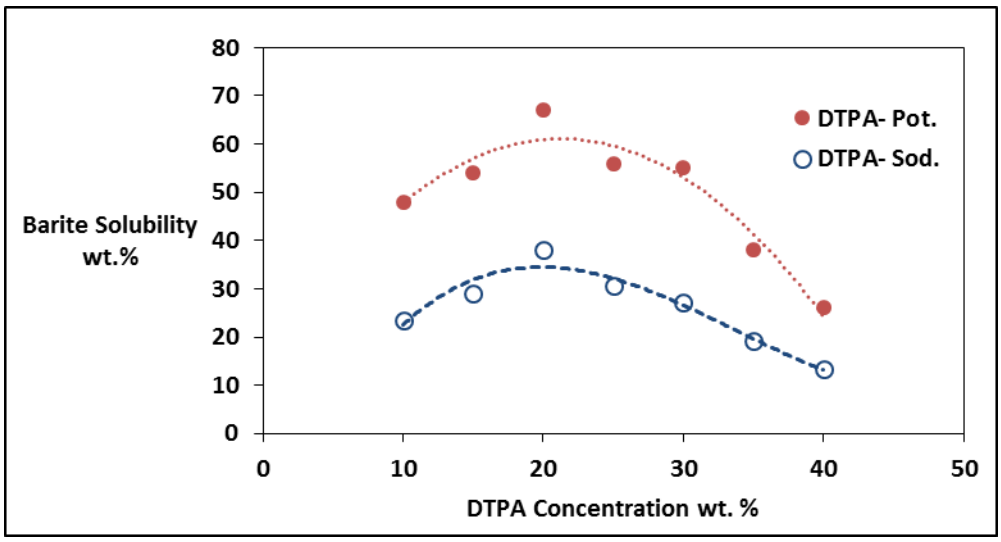


Figure 19 Barite Solubility (in percentage) with DTPA- Potassium/ Sodium Base (pH 11 -12; Temp: 200 °F; Duration: 24 hrs)

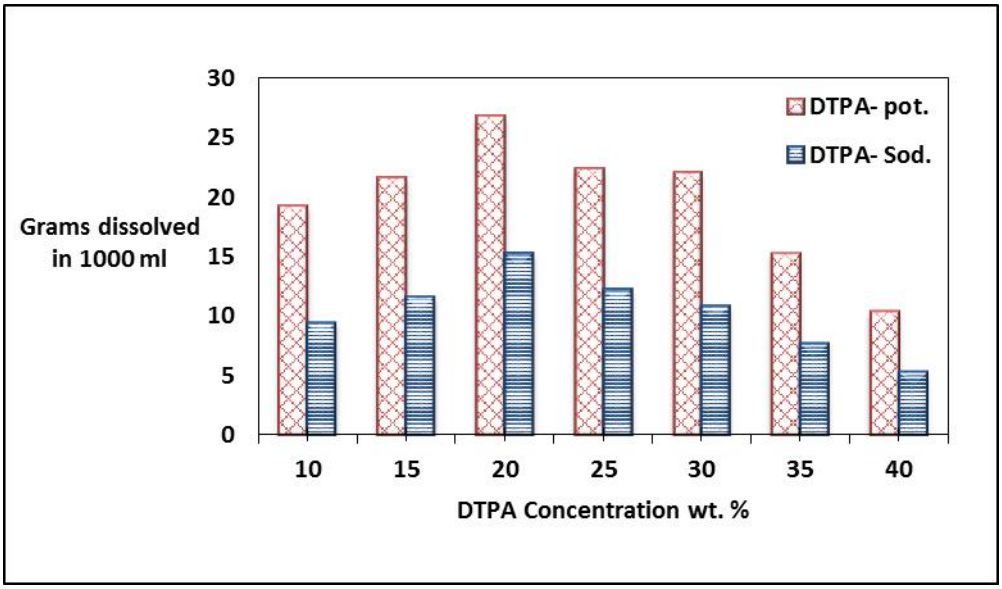


Figure 20 Comparing DTPA potassium/ sodium base solubility in grams per liter (pH 11 -12; Temp: 200 °F; Duration: 24 hrs)

The solubility of DTPA powder is limited in water so adding of KOH is required to increase the solubility. This also helps in increasing the pH. 1.3M of KOH (Mw 56.11) solution was found to be sufficient to make the 20 wt% concentration of DTPA with pH around 3.5 as shown in Figure 21. The required concentration of KOH needed to prepare certain pH of 20 wt% of DTPA solution is shown in Figure 21. As the pH of the solution reaches a value higher than 12.5, the DTPA becomes fully deprotonated and less sensitive to the concentration of KOH.

The dissolution capacity of industrial barite particles increases by increasing the pH of 20 wt% DTPA potassium base, Figure 22. The barite solubility reached the maximum at pH greater than 11 which is prepared by 3.5M of KOH. It was noted that increasing the KOH concentration from 3.5 to 4.5M (to obtain pH > 11) has no effect on the barite dissolution with 20 wt% DTPA. Higher concentration of the KOH, more than 4.5M, has a reverse effect on barite dissolution rate in the 20 wt% DTPA. Therefore, for preparing DTPA penta potassium using DTPA powder, it is recommended to keep the KOH concentration in the range of 3.5 to 4.5M to achieve the maximum barite dissolution.

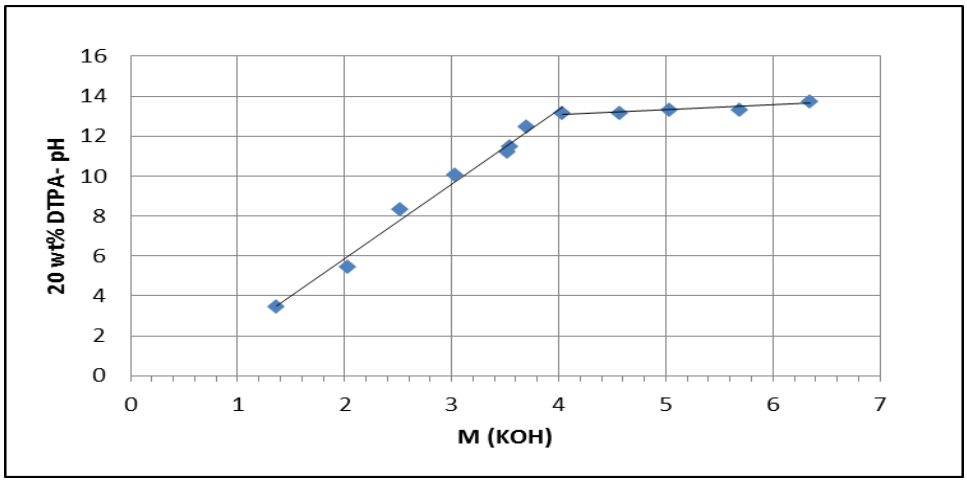


Figure 21 Molarity of KOH to prepare DTPA 20 wt%.

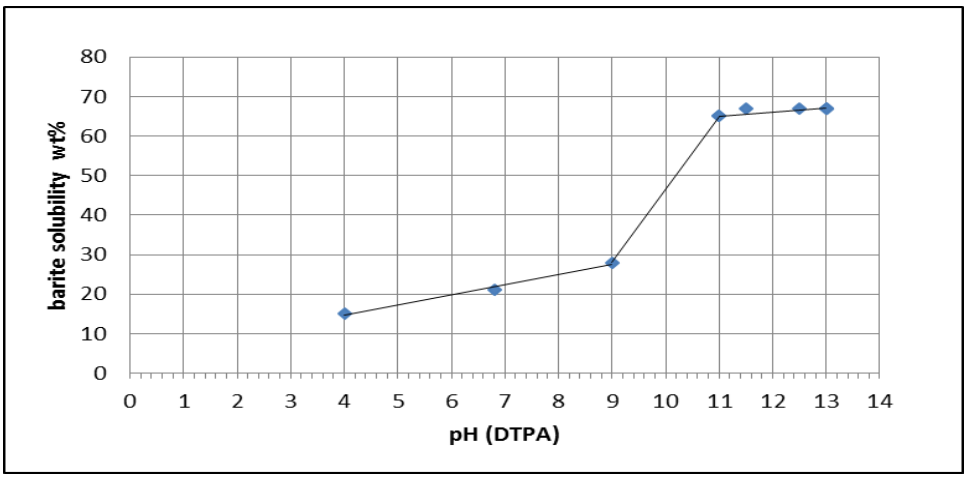


Figure 22 Effect of pH on barite solubility (Temp: 200 °F; Duration: 24 hrs)

The rate of the dissolution of Ba^{2+} from $BaSO_4$ using chelating agents is affected by several resistances based on concentration of the chelating agent and the pH of the solution [47]. At low pH, where the chelating agent exists in the acid form, the presence of Hydrogen ions compact the chelating agent and minimize the dissolution of $Ba^{2}+$. The chelating ability is increased by increasing the pH and reaches the maximum for fully deprotonated chelating agent. In our case, at high pH, higher than 11, the dissolution is affected by the concentration of DTPA in the solution. At low concentration of DTPA, lower than 15 wt. %, the driving force between the bulk concentration of DTPA in solution and to that on the surface of barite is low. Therefore, the rate of dissolution is mainly controlled by mass transport of DTPA. However, at high concentrations, this effect is negligible compared to the effect of the adsorption of DTPA on the surface of barite and solution complexation reaction thereafter. Therefore, the DTPA is first adsorbed on to the surface followed by solution complexation reaction between DTPA and BaSO4 according to the following equation:

$$HY^{-4} + OH^{-} \rightleftharpoons Y^{-5} + H_2O \qquad (5.3)$$

$$BaSO_4 + Y^{5-} \rightleftharpoons BaY^{3-} + {SO_4}^{2-} \qquad (5.4)$$

$$BaSO_4 + HY^{4-} + OH^{-} \rightleftharpoons BaY^{3-} + {SO_4}^{2-} + H_2O \qquad (5.5)$$

Higher concentration of DTPA, greater than 25 wt.%, leads to a decrease in the rate of dissolution due to increasing competitive adsorption of DTPA on the surface of barite and hence decreasing the rate of desorption of $Ba^{2}+$ into the solution (increasing desorption resistance of Ba^{2+}). Moreover, When increasing the concentration by more than 20 wt. % of DTPA increases the viscosity and retards the reaction [48].

The stability of the solution after the solubility test was monitored for one hour after the test. The stability test gives another confirmation that 20wt% DTPA-K_5 is the most stable concentration because it was able to hold the soluble barite in the solution. Figure 23 shows that there was a precipitation of barite solids in the solution after 1 hour. This precipitation increases with increasing the DTPA concentration. The concentration range of 20% to 25 wt% was the most stable with time. Monitoring these solutions for longer times up to 48 hours showed that the 20 wt% yielded a constant stability.

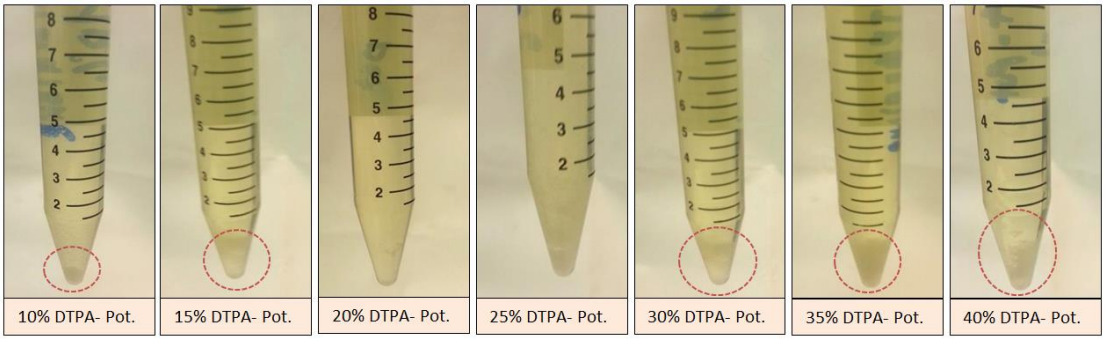


Figure 23 Stability of DTPA solution with time

The above results were conducted based on 24 hours solubility test. Therefore, the effect of time on the dissolution rate of barite in 20 wt% DTPA-K_5 was tested here. The relationship between the industrial barite solubility in the 20wt% DTPA pentapotassium and time indicated that there was a significant increase in the percentage of barite solubility at the time period up to 24 hours. The maximum value of barite solubility was 67% at 24 hours. After that the dissolution rate of barite in DTPA remained almost the same in the range of 67% up to 70% with time, Figure 24. Based on this result, the 24 hours can be taken as the optimum time to achieve good barite solubility. Increasing the time for more than 24 hours is not recommended due to the minor impact on the barite dissolution beyond this time.

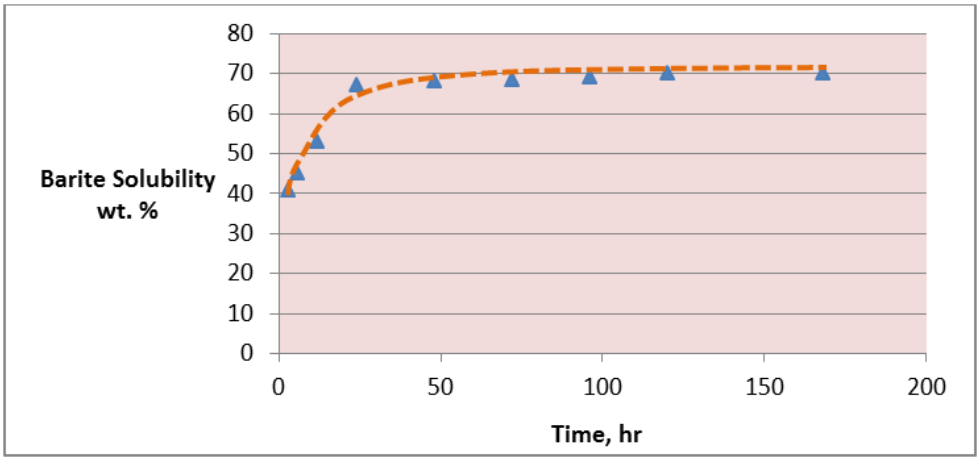


Figure 24 Relationship between time and Barite dissolution in 20% DTPA-K_5 (Temp: 200 °F)

5.4.2 Solubility of Barite in EDTA

The EDTA sodium base solutions can be prepared using the NaOH from the EDTA powder ($C_{10}H_{16}N_2O_8$). EDTA tetra sodium (**EDTA-Na_4**) was available at 39 wt% aqueous solution. The results show that the maximum dissolution capacity of the industrial barite solids was around 26% using 20 wt% of EDTA-Na_4 as shown in Figure 25. The pH of the EDTA-Na_4 solution was 12 and the test was conducted for 24 hours at 200°F.

The other type of EDTA sodium base was EDTA disodium (EDTA-Na_2 98-100% powder; $C_{10}H_{14}N_2Na_2O_8.2H_2O$). The disodium EDTA solution was prepared using distilled water and NaOH. The solubility of EDTA disodium (**EDTA-Na_2**) in water was limited so the pH of the solution was increased by the NaOH. The lowest pH value where the EDTA disodium becomes soluble is around 8.5 pH. The dissolution of the solids was very small in EDTA disodium with concentration ranging from 10% to 30 wt%. The maximum dissolution capacity of the solids was around 6% using 20 wt% of EDTA-Na_2 in 24 hours at 200 °F.

Dipotassium EDTA-K_2 (99% Powder) was used to prepare different concentrations of EDTA-K_2 to evaluate the barite dissolution rate. The Dipotassium EDTA 20 wt% is soluble in water at pH around 5. At this condition the solubility of barite was limited in EDTA-K_2; the barite solubility reached 10% as maximum value using 20 wt% EDTA-K_2 in 24 hours.

The potassium base EDTA-K_4 was prepared using EDTA powder ($C_{10}H_{16}N_2O_8$) and the KOH water solution. The results of EDTA-K_4 potassium base is shown in Figure 25. 20 wt% of EDTA-K_4 dissolved 64% of the barite. Altering the base of EDTA from sodium

to potassium using KOH enhanced the solubility of industrial barite by 38% from 26% to 64 wt%, Figure 25. The capacity of barite dissolution reached 25.6 gm per litter by using potassium base EDTA compared to sodium base, Figure 26.

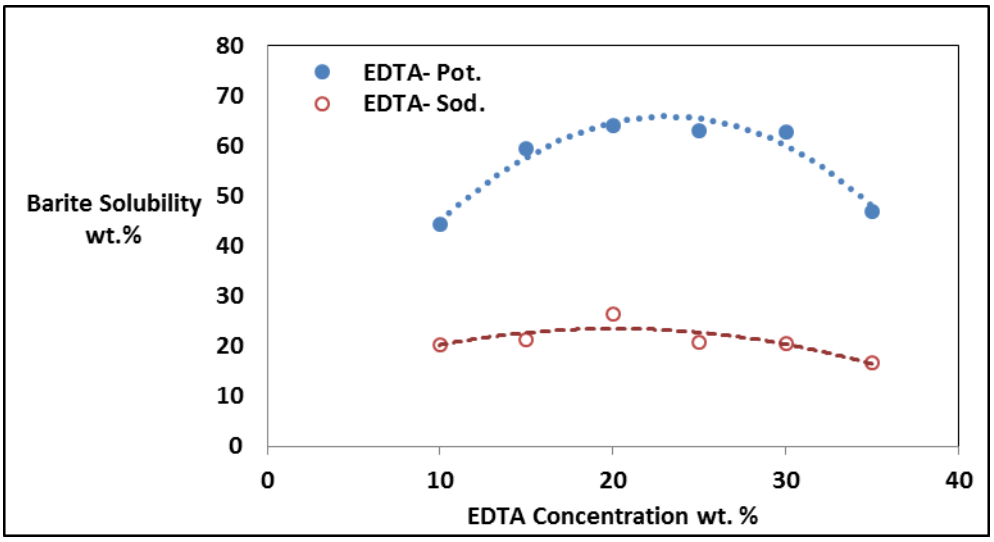


Figure 25 Barite Solubility (in Percentage) with EDTA- Potassium/ Sodium Base (pH 11 -12; Temp: 200 °F; Duration: 24 hrs)

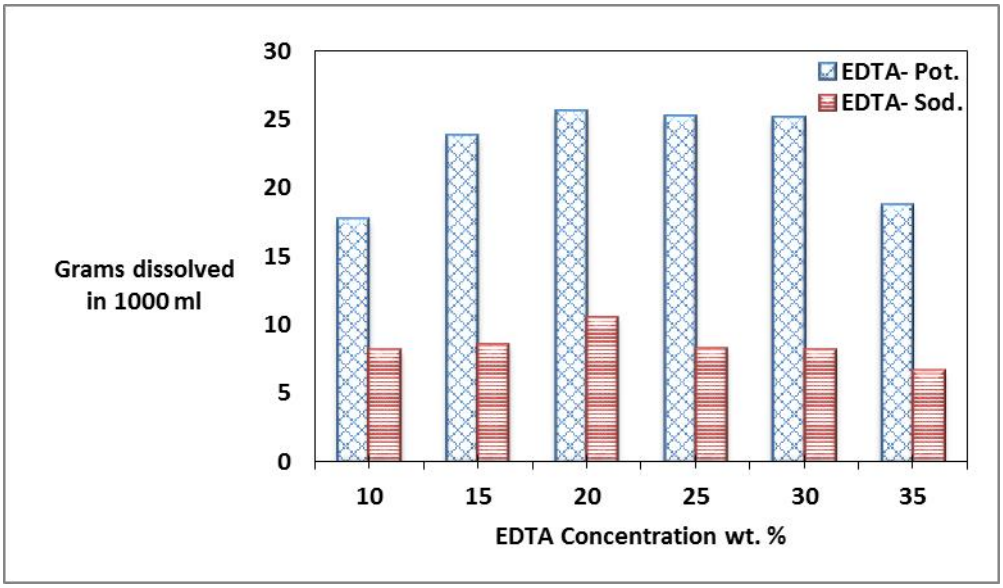


Figure 26 Comparing EDTA potassium/ sodium base solubility in grams per liter (pH 11 -12 at 200 °F, 24 hrs).

1.7 M of KOH (Mw 56.11) solution is sufficient to make 20 wt% concentration of EDTA powder soluble in distilled water with a pH of 4.8 as shown in Figure 27. The required concentration of KOH needed to prepare a 20 wt% of EDTA solution of a certain pH with is shown in Figure 27. Using KOH solution with concentrations ranging from 4M to 5M is sufficient to prepare EDTA 20 wt% with pH ranging from 11 to 12.5. Increasing the concentration of KOH solution more than 5M is not recommended to prepare the EDTA solution from the point of view of dissolution of barite.

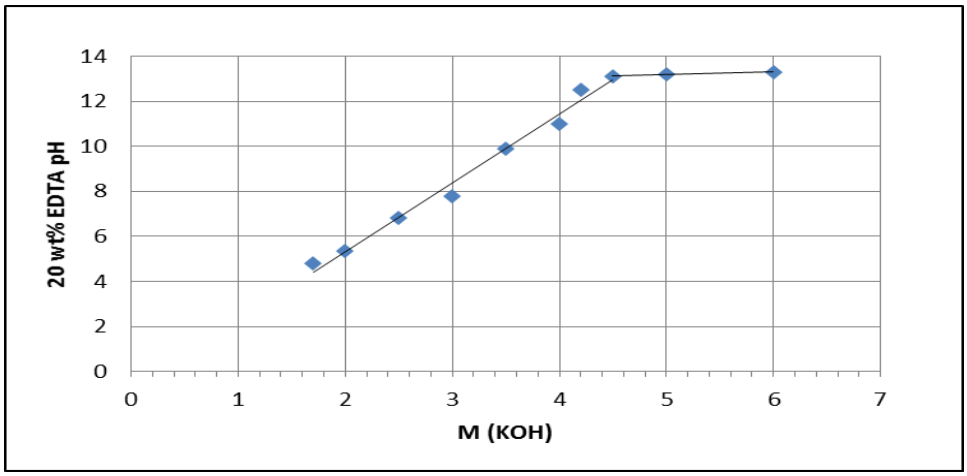


Figure 27 Molarity of KOH to prepare EDTA 20 wt%.

5.4.3 Solubility of Barite in HEDTA

The dissolution rate of industrial barite was evaluated using sodium base Hydroxy ethylethylene diamine triacetic acid (HEDTA-Na_3) at high pH. The results show that the dissolution of barite particles in HEDTA was low. The optimum concentration of HEDTA is 20 wt% where 6.5 gm of barite was soluble in one litter of 20 wt% HEDTA-Na_3.

5.4.4 Solubility of Barite in GLDA

Two types of GLDA sodium base high pH (11-12) and low pH (3.5) were used to evaluate the dissolution rate of barite. It was found that the barite gave zero solubility in the GLDA at both low and high pH.

5.5 Characterization of Barite before and after Solubility Using DTPA-K_5

5.5.1 SEM, XRD and Particle Size Analysis

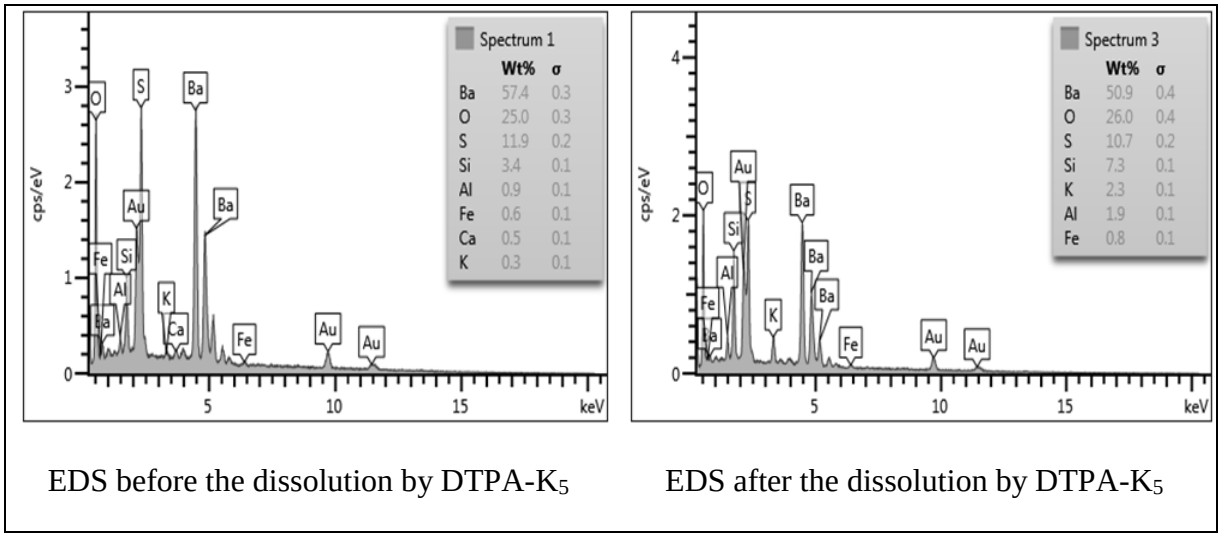
The solubility experiments showed that DTPA-K_5 and EDTA-K_4 were the most effective chelating agents in dissolving barite. Several analyses were conducted to understand the mechanism of the dissolution of barite in DTPA-K_5. The SEM-EDS analysis for the barite was conducted in different Spectrum to cover variable sites of the same sample. **Error! eference source not found.**28 and 29 shows the chemical composition of the industrial barite used in this work before and after the dissolution in DTPA-K_5. The data presented

that the main element is barium and sulfur which form Barium sulfate (**$BaSO_4$**). Based on EDS data, the impurities including (Si, Al, Ca and others) was ranged from 5% to 7 wt% in average of all Spectrums. Although the EDS result showed that the purity of the barite is around 94%; the XRD considered the purity of the barite as 99-100 wt% as shown in Figure 30. The impurities were not observed by XRD. X-Ray Diffraction analysis for the Barite sample before and after treatment is shown in Figure 30 and Figure 31. Untreated sample demonstrated 10 major peaks related to pyrite crystalline phases. These peaks appeared at 20.46 2θ (011), 22.79 2θ (111), 24.87 2θ (002), 25.86 2θ (210), 26.85 2θ (102), 28.75 2θ (211), 31.53 2θ (112), 32.81 2θ (020), 42.59 2θ (113) and 42.93 2θ (122). Upon treatment the intensity of these peaks reduced by 50% and become wider which lead to more amorphous phases.

The particle size results indicated that the industrial barite used in this study has a narrow distribution with mean particle size ranged from 30 to 40 micron, Figure 32. The 200µ scale SEM high resolution picture in Figure 29 shows that the majority of the barite particles have sharp edge and most of the particles have a size of 30 to 50 micron. This observation about the particle size of the industrial barite using SEM confirmed the collected data from the particle size distribution analysis.

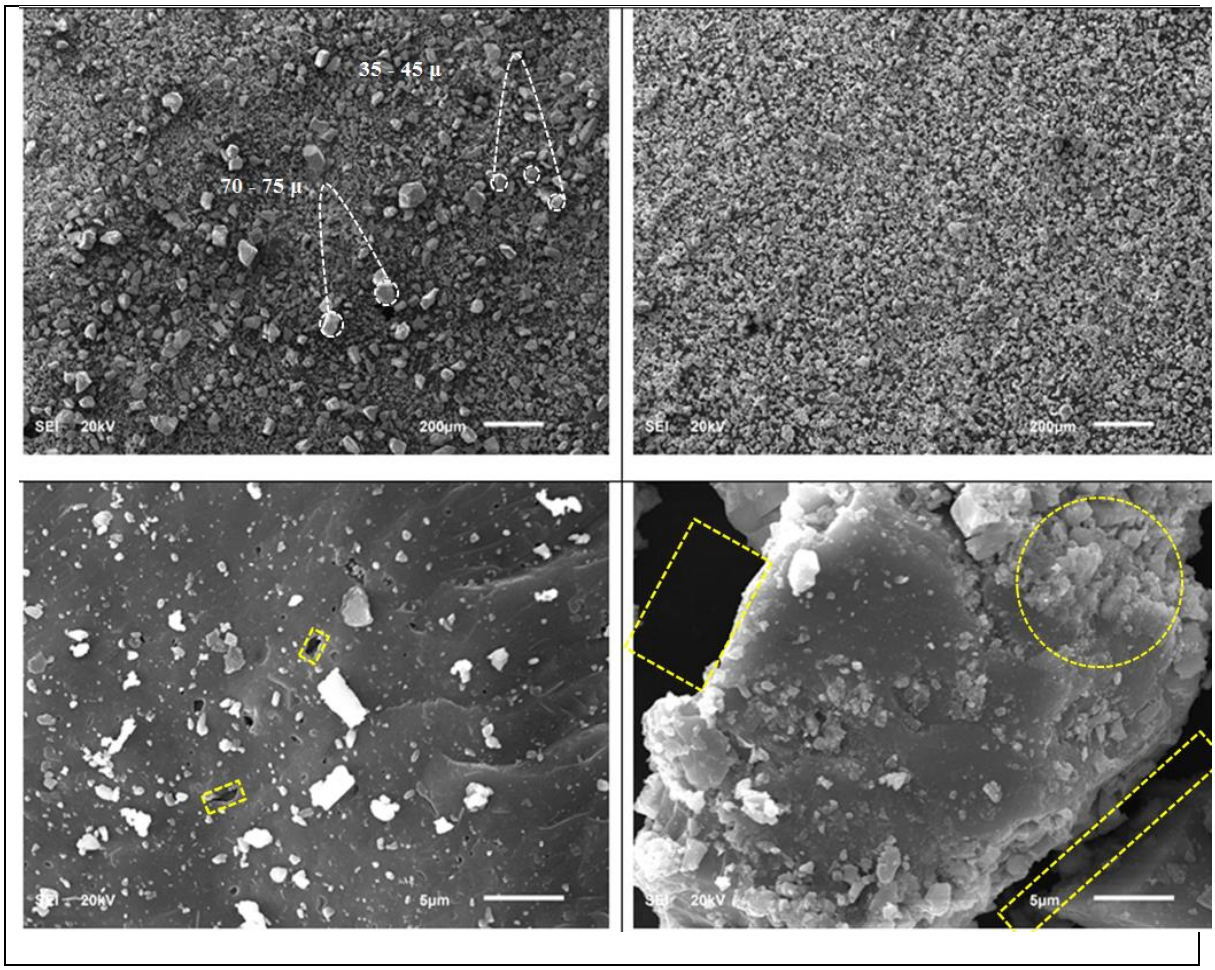
The lower scale picture (5µ) focuses on one particle to display the size of the pores in the barite particles The pore size of the barite particles was found to be around 2-3µ in length and 1-2µ width. The pores size on the surface of the barite particles increased due to the dissolution of DTPA-K_5 which increased the area of the reaction and the dissolution rate. The composition of the solid remaining after the dissolution was analyzed to evaluate the precipitated solids. The EDS showed that the precipitated solids contained only barium

which indicated that no new composition formed and the precipitate was barite, Figure 28. The appearance of potassium was due to the base of the DTPA (potassium base). The XRD results of the precipitated showed that there is quartz (SiO_2) formed during the dissolution test, Figure 31.



EDS before the dissolution by DTPA-K_5 EDS after the dissolution by DTPA-K_5

Figure 28 SEM (EDS) analysis of Barite solids before and after the dissolution in DTPA-K_5



SEM high resolution picture for barite particles before the dissolution by DTPA-K_5 200µ, and 5µ	SEM high resolution picture for barite particles after the dissolution by DTPA-K_5 200µ, and 5µ

Figure 29 SEM high resolution picture for barite particles before and after dissolution with DTPA-K_5

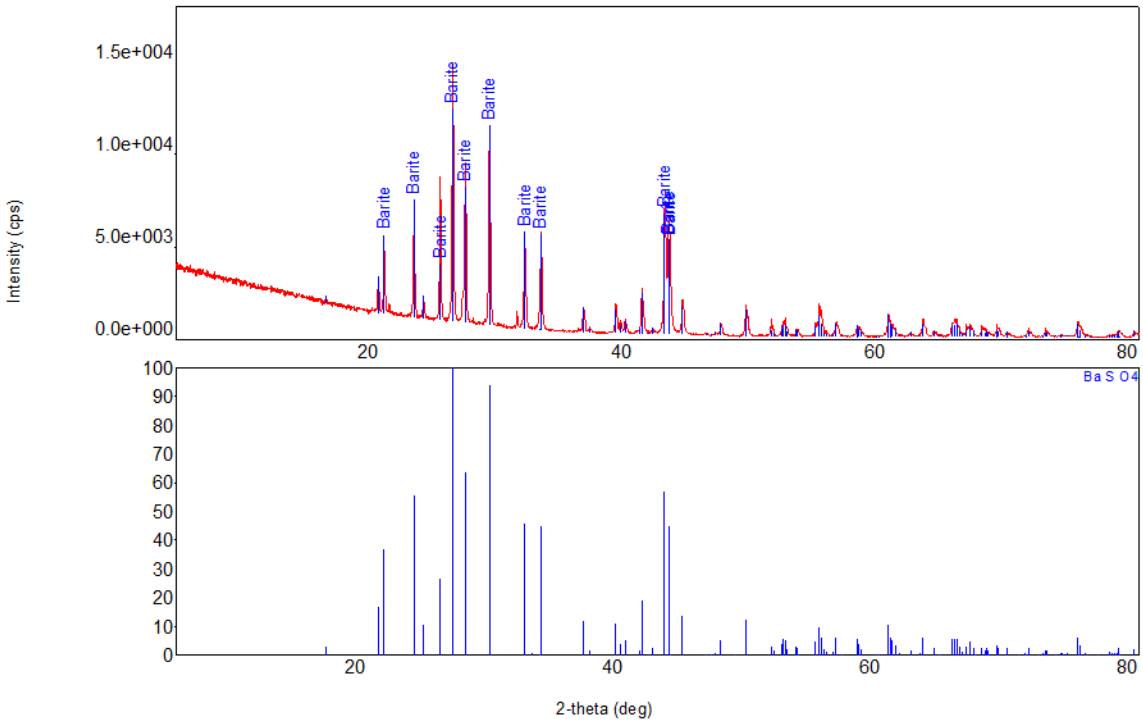


Figure 30 XRD analysis of Barite solids used in this work before the dissolution

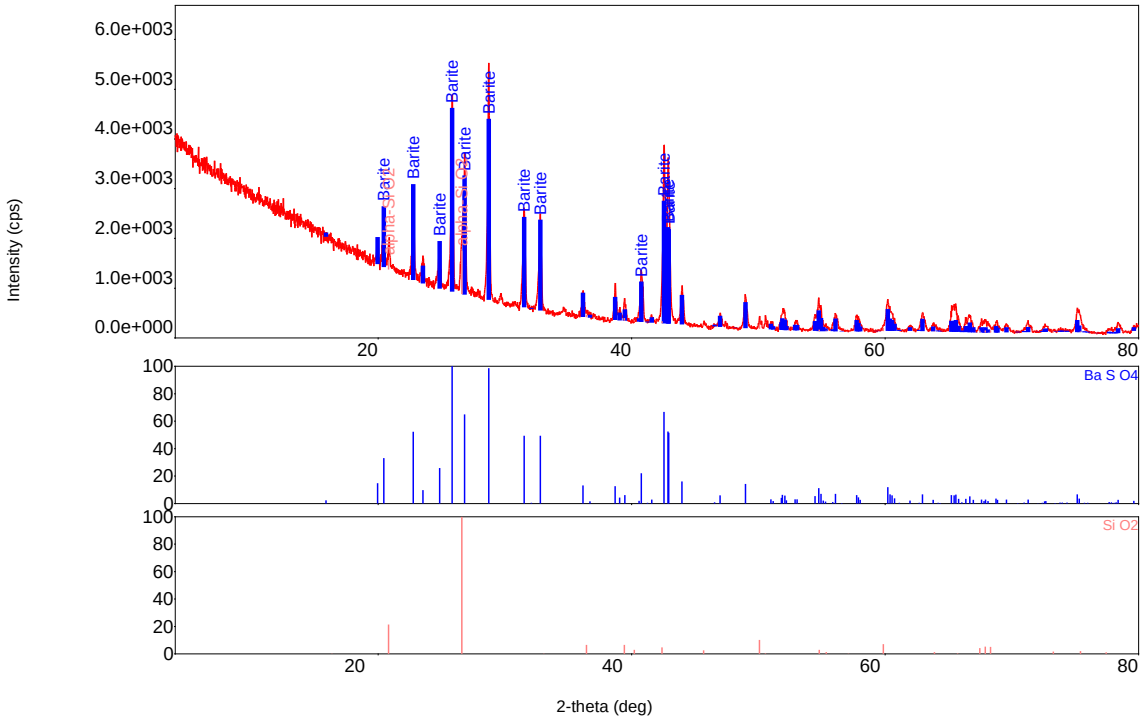


Figure 31 XRD analysis of Barite solids used in this work after the dissolution

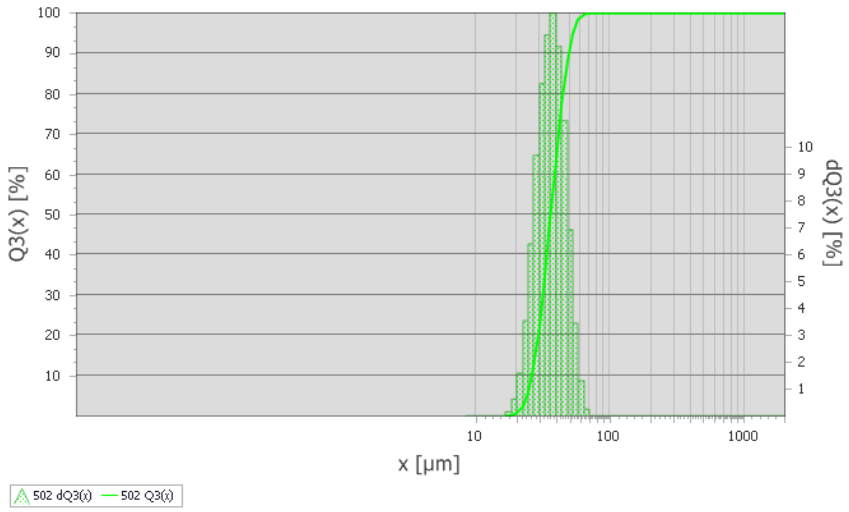


Figure 32 Particle size distribution of industrial barite solids

5.5.2 FTIR analysis

The upper section of Figure 33 shows the FTIR spectroscopy for the barite solids before the dissolution whereas the FTIR for the solids remaining after the solubility with DTPA-K_5 is shown in the bottom section Figure 33. Table 2 shows that the major FTIR absorption bands for barite solids before (**BSB**) and barite solids after the dissolution (**BSAD**) can be divided into seven groups depending on the different frequencies of the band position. The comparisons between the FTIR peaks for BSB and BSAD and possible assignments for each peak are present in Table 2. There are four fundamental vibrational modes of sulphate bands called; non degenerate (v_1), one doubly degenerate (v_2), and two triply degenerate (v_3 and v_4) [49–54].

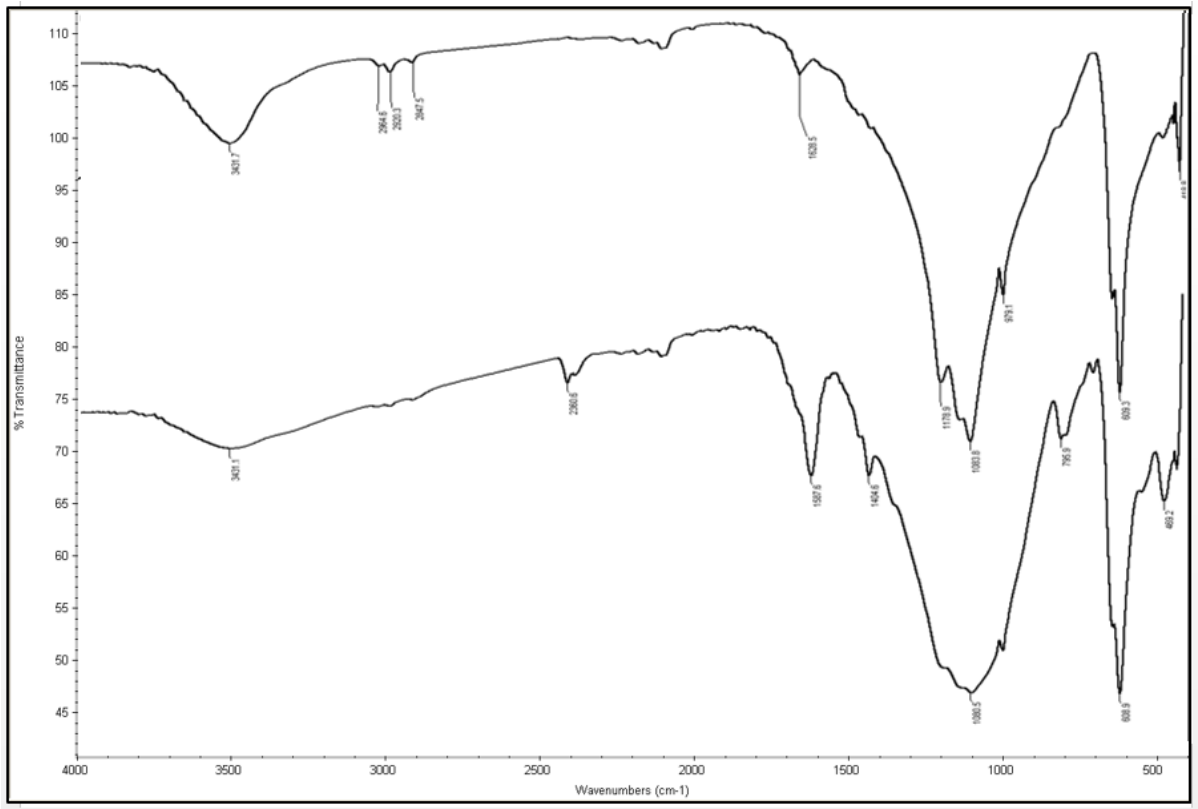


Figure 33 FTIR analysis for barite particles before and after the dissolution with DTPA-K_5

Table 2 Infrared band positions of the studied barite

Wave number (cm^{-1})			Assignments
Peaks group	**Before**	**After**	
Group A	3431.7	3431.1	H-O-H stretching
Group B	2964.6	-------	CH stretch
	2920.3	-------	CH stretch
	2847.5	-------	CH stretch
		2360.6	KBr disc
Group C	1628.5	-------	H-O-H bending
	-------	1587.6	of water
	-------	1404.6	N-H amine group
Group D	1178.9	-------	(v_3) sulfate vibrational modes
	1083.8	-------	(v_3) sulfate vibrational modes
	-------	1080.5	(v_3) sulfate vibrational modes
	979.1		(v_1) sulfate vibrational modes
Group E	-------	795.9	Si-O-Si stretching
Group F	609.3	606.9	(v_4) sulfate vibrational modes
Group L	419.9	-------	"Al-OH" translation
		469.2	(v_2) sulfate vibrational modes

FTIR spectroscopic analyses for the BSB and BSAD solid materials showed that the dissolution of barite particles in DTPA-K_5 affected the bands position and the absorbance intensity. Group-A shows two bands at 3431.7cm^{-1} in BSB and 3431.1 cm^{-1} in BSAD, which signifies the presence of O–H stretching mode of hydroxyl groups and absorbed water [55,56]. The peak 3431.1 cm^{-1} in BSAD becomes broader after the dissolution and the absorbance intensity of this peak was decreased when the barite was dissolved in DTPA-K_5 (potassium hydroxides base). In group-B the peaks at 2964.6, 2920.3 and 2847.5cm^{-1} appeared in BSB with very low intensity which are related to CH stretch [56,57]. These peaks are completely disappeared after the dissolution. The peak at 2360.6cm^{-1} in BSAD was appeared which is not diagnostic of any mineral in the used barite sample and it showed due to the use of KBr in the sample preparation for FTIR [54].

On the other hand, in group-C the peak at 1628.5in BSB is subsequent to a slight amount of water being present in barite crystal [52]. The intensity of this peak increased and shifted to 1587.6cm^{-1} in BSAD as an indication of the capability of barite to absorb water increased due to the dissolution of barite solids in DTAP [56,58]. The new peak at 1404.6cm^{-1} was found only in BSAD, which indicated the presence of N-H bending in the amine group created by using the DTPA.

In group-D the peaks at 1178.9 and 1083.8 cm^{-1} in BSB are related to the third vibrational modes (v_3) of sulfate [50] and peak at 979.1 cm^{-1} is assigned to the (v_1) vibrational modes of sulfate [51]. These peaks were diminished and a new peak appeared at1080.5 cm^{-1} in BSAD as a result of the dissolution of barite in DTPA-K_5. The new peak at 1080.5 is cm^{-1} is attributed to (v_3) sulfate vibrational mode [50,51]. The decrease of the 1080.5 cm^{-1} peak intensity means that some of the sulfate functional groups were removed due to the

dissolution. The new peaks at 795.9 cm^{-1} related to Si-O-Si group [59]. This peak confirmed the SEM results where the Si wt% percentage increases after the dissolution of barite in DTPA. The peak at 609.3 cm^{-1}, which is related to the (v_4) vibrational modes of sulfate, was shifted to 606.9 cm^{-1} with same intensity for the same vibrational mode [50,51]. This was an indication that the v_4 vibrational mode of sulfate was not easily to break during the dissolution of barite. The peak at 419.9cm^{-1} refers to the presence of the Al-OH translation modes in BSB [60]. The "Al" was showed also in the SEM results as one of the impurities in the industrial barite used in this study. The intensity of this peak was decreased as result of the dissolution of barite in DTPA. The peak at 469.2cm^{-1} in BSB was appear in low intensity and in the BSAD it displayed as an indication of (v_2) sulfate vibrational modes [51,52,61].

5.6 Summary

Based on the results obtained from this study to evaluate the dissolution rate of the industrial barite particles in different chelating agents at a high temperature (95° C, 200 °F); the following conclusions can be drawn:

- Potassium base DTPA-K_5 and EDTA-K_4 at 20 wt% concentration provided the maximum barite dissolution capacity, viz., 26.8 g/L and 25.6 g/L at 24 hours, respectively.
- The recommended pH of DTPA-K_5 and EDTA-K_4 should be greater than 11 to achieve the maximum solubility of barite.

- At high pH, the dissolution of barite is controlled by the adsorption of DTPA on surface and the solution complexation reaction thereafter.
- Using sodium base DTPA, EDTA, and HEDTA with high or low pH is not recommended to dissolve barite.
- The barite dissolution rate in chelating agents DTPA-K_5 and EDTA-K_4 increases with time up to 24 hours. The soaking process after 24 hours has a minor effect on barite dissolution. .
- The FTIR results showed high capability of the DTPA potassium base to break the v_3 and v_1 sulfate vibrational modes; however, the v_4 sulfate vibrational mode was hard to break during the dissolution.
- The original barite consisted of v_1, v_3 and v_4 vibrational sulfate modes. After dissolution, the barium sulfate was found to be in v_2 and v_4 vibrational sulfate modes. The v_2 mode was formed during the dissolution.
- The dissolution capacity of other chelating agents was found to be as follows: DTPA-Na_5 (15.2 g/L), EDTA-Na_4 (10.5 g/L), HEDTA-Na_3 (6.7 g/L), GLDA-Na_4 (zero), EDTA-K_2 (4 g/L), and EDTA-Na_2 (2.4g/L) in 24 hour soaking time at 95°C.

CHAPTER 6

SINGLE STAGE FILTER CAKE REMOVAL OF BARITE WEIGHTED WATER BASED DRILLING FLUID

The removal of barite filter cake is a challenging problem because the conventional filter cake removal treatments that use hydrochloric acid (HCl) or chelating agents were ineffective in dissolving barite containing filter cakes. Barite, or barium sulfate, is insoluble in water and acids such as HCl, formic, citric, and acetic acids. Also barite has very low solubility in chelating agents such as Ethylene diamine tetra acetic acid (EDTA) and Diethylene triamine penta acetic acid (DTPA).

The present study focuses on developing new formulation to remove the barite filter cake. The removal formulation consists of chelating agents such as Diethylene Triamine Penta acetic Acid (DTPA), converting agent or catalyst, and polymer breaker (Enzyme). Solubility tests of industrial barite and solids collected from de-sanders during well flow back were conducted to develop barite removing solvent. Actual barite drilling fluid samples were collected from the field during drilling a high pressure high temperature deep gas well. The performance of the designed formulation was examined to remove the filter cake formed by real drilling fluid samples collected during drilling operations using High Pressure High Temperature cell (HPHT).

Based on the result of this work the filter cake removing formulation dissolved more than 90% of the filter cake formed by real barite drilling fluid in a single stage within 24 hours. The removal formulation consists of high pH potassium base DTPA of 20% wt

concentration, enzyme as a polymer degrading agent, and one of the following converting/catalytic agents (potassium carbonate, potassium formate, or potassium chloride). The use of converting agents increased the barite solubility from 67% to 95%.

6.1 Introduction

The drilling fluid must counter or suppress formation pressure. Therefore, the drilling fluid has to have enough density to balance the formation pressure and to keep the wellbore stable. For this reason, weighting materials such as barite, iron oxides, manganese tetraoxide, potassium formate, hematite, and calcium carbonate are used in the drilling fluid to achieve the required mud density [1]. In deep oil and gas wells, barite is the most common for its desirable density, low production costs, and ease of handling.

For a filter cake to form, the drilling fluid must contain some particles of a size only slightly smaller than the pore openings of the formation [62]. These particles are known as bridging particles and are trapped in surface pores, thereby forming a bridge over the formation pores. Filter cake building fluids can also contain polymers for suspension of solids and for reducing liquid loss through the filter cake by encapsulating the bridging particles [31,63]. Polymers can be either natural or synthetic polymers. The polymers can include one polymer such as xanthan to enhance rheological properties [64,65] and a second polymer, a starch for example to reduce fluid loss [66,67]. At completion of the drilling, however, the filter cake must be removed to allow production of the formation fluids or bonding of cement to the formation at the completion stage. Removal of the deposited filter cake should be as complete as possible to recover permeability within the formation [68].

The composition of the formed filter cake over the face of the formation depends on the composition of drilling fluid solids additives, properties of the drilling fluid, the drilled formation mineralogy, the differential pressure, and other factors [2,5,6,10,11,16]. The weighting material contributes in average with 70 to 90% wt of the filter cake mineralogy (Ba geri et al., 2013a). During the removal of the filter cake the main focus was to dissolve the weighting material. The filter cake removal conducted in two stages, the first stage is to break the polymer coat formed by starch or XC polymer [69]. The polymer degrading enzyme is used in this stage with a concentration of 10% wt. The second stage is to dissolve the weighting material of the filter cake using the conventional filter cake removals such as hydrochloric acid solution, chelating agents, and others [33,70]. The reason behind using two stages filter cake removal is the incompatibility between the polymer degrading enzyme used in the first stage and the filter cake breaker in the second stage [33].

Several previous studies were conducted on different types of filter cake removal formed by different types of drilling fluid. For example the filter cake formed by manganese tetraoxide was removed by HCl, citric, in-situ lactic acid or by using a combination of HCl and organic acid [33,71]. Glutamic diacetic acid (GLDA) was presented as an environmentally friendly fluid to remove the filter cake formed by calcium carbonate mud in one step without using enzyme [70] as well as two stage of removal using enzyme and poly-lactic acid [72]. Oxidizers also were used to remove the calcium carbonate damage [73]. However, the removal of barite containing filter cakes has been a challenging problem, since the conventional filter cake removers did not work properly in barite removal. Removal treatments utilizing an oxidizer (e.g. persulfate), hydrochloric acid solution, organic (acetic, formic) acid, or a combination of acid and oxidizer, were effective

in removing other types of drilling fluid's filter cakes, are ineffective in dissolving barite containing filter cakes. Barite, or barium sulfate, is insoluble in water or acid [38,40]. Barite solvents such as DTPA and EDTA were introduced previously and the maximum reported dissolution or removal efficiency was 60% wt [37–39,74–77].

The DTPA chelating agent was introduced as the most effective solvent for barite, however still there is a need to evaluate the efficiency of DTPA to dissolve the barite in presence of other drilling fluid solids and find a way to increase the dissolution capacity of DTPA by using catalyst or converting agents that will be targeted in this work.

Therefore, an urgent need exists in the drilling and completions sector for a fluid that can remove the barite filter cake efficiently. In gas wells the filter cake usually is not removed in open hole completion and the barite particles will be produced with the gas. Oil companies found out that, the produced barite particles with the gas eroded the surface chokes and valves. Based on that, the main objective of this work is to address a solution that is competent to remove the filter cake formed by drilling fluid using barite drilling fluid with high removal efficiency. In order to achieve the main goal of this work the following objectives will be studied respectively: (1) Using high temperature solubility system to test and calibrate the optimal concentration of different bases of DTPA that can achieve the maximum solubility of barite particles, (2) After that, different enzymes with different concentrations will be examined to evaluate their compatibility with DTPA and impact on the dissolution of barite particles, (3) Study the effect of different catalysts (converters) with various concentrations added to the obtained formulation in part (1) on the rate of barite dissolution, (4) Study the dissolution rate of barite in the solution formulation obtained as function of time and temperature, (5) Check the designed

formulation efficiency by testing the solubility rate of drilling fluid solids collected after separation process in the field, (6) Evaluate the barite filter cake removal efficiency using HPHT filtration test using the developed formulation.

6.2 Materials and Experimental Work

6.2.1 Materials

Industrial barite (barium sulfate) grade was used to perform the solubility experiments. The barite particles were sieved using 75 micron mesh size to obtain particle size less than 75 micron.

Real water-based mud (collected from a drilling rig from one of the deep gas wells, Middle East) was used to form the filter cake in HPHT cell.

Table 3 shows the drilling fluid formulation used in this study. The barite particles present in the drilling fluid system as the main weighting material. The amount of barite used in this drilling fluid system was 352 lb out of total solids weight (451.8 – 453.3 lb) with an approximate percentage of 80% of the total solids. The bentonite clays was used to improve hole cleaning by high carrying cutting capacity, control drilling fluid rheological properties and others [63,78]. Xanthomonas campestris (XC polymer), also known as xanthan gum, was used to enhance the drilling fluid rheology, and cutting transportation as well as to control the fluid loss [11,69]. The other salts are commonly used in the water based drilling fluid such as KOH to control the pH, Sodium sulfite as an oxygen scavenger [71], Calcium Carbonate ($CaCO_3$) medium as a bridging agents and KCl to control the clay. Other solids

were added to the drilling fluid in small quantities (less than 1% of the total drilling fluid solids). These solids are; BARANEX as filtration control agent, Soltex to stabilize shale formations, BlackNite to prevent stuck pipe, and SOURSCAV as hydrogen sulfide scavenger.

Solids collected from de-sanders during well flow back were also used in this study to test the solubility of the drilling fluid solids in the removal formulation. The basic drilling fluid properties of the used mud are listed in Table 4.

Diethylene Triamine Pentaacetic Acid (DTPA) two bases, potassium salt (K_5-DTPA) and sodium salt (Na_5-DTPA) were used in this study as the main composition of the barite filter cake removal formulation. The initial concentration of the DTPA was 40% wt in an aqueous solution.

Three different types of ultra-high temperature stable enzymes, Alpha Amylase (enzyme A), Endoglucanase (enzyme B) and mannans (enzyme C), were used as polymer removal agent. The used enzymes were almost pure (97 – 100%). To enhance the dissolution of the barite in the DTPA, several converting agents such as potassium carbonate, potassium chloride, potassium formate, potassium nitrate, ammonium carbonate, ammonium chloride, calcium chloride, magnesium chloride, and sodium carbonate were added to the solution.

Table 3 Drilling Fluid Formulation

Name	Unit	Description	Weight%
Water	bbl	0.691	34.78
Bentonite	lb	4	0.57
XC-polymer	lb	0.5	0.07
BARANEX	lb	0.25-0.50	0.07
KCl	lb	20.0	2.87
KOH	lb	0.5	0.07
NaCl	lb	66	9.48
Barite	lb	352.0	50.56
$CaCO_3$ medium	lb	5.0	0.72
Sodium sulfite	lb	0.25-0.30	0.04
Soltex	lb	1.0-2.0	0.14
BlackNite	Gal	0.3-0.5	0.32
SOURSCAV	lb	2	0.29

Table 4 Drilling Fluid Properties

Name	Unit	Description
Density	lb/ft^3	120
PV	cP	30-40
YP	$lb/100\ ft^2$	24-26
10 sec gel	$lb/100\ ft^2$	10-20
10 min gel	$lb/100\ ft^2$	15-25
Filtrate, HTHP @320°F/500 psi	ml/30min	18-24
HTHP Cake	32^{nd} in	1-3
pH		9-10

6.2.2 Experiments

Solubility Tests

In the first stage of the experiments, the solubility of the industrial barite (barium sulfate) grade in K_5-DTPA and Na_5-DTPA was evaluated at (200°F). The solubility experiments were conducted under constant stirring rate (350 rpm) using flask connected to reflux condensers to ensure no water loss at high temperature (200°F). 4 gm of the industrial barite was mixed in 100 ml of the solution (e.g. DTPA or DTPA with catalyst) to measure the solubility for 24 hours soaking time. At the end of the test after 24 hrs the mixture was filtered using 2 micron filter paper and the remaining barite weight (insoluble) was determined. The difference between the initial barite weight (at the start of the test) and remaining barite weight after 24 hrs (at the end of the test) is the dissolved barite weight during the test. The solubility was determined by the following equation:

$$solubility\% = \frac{dissolved\ barite\ weight}{initial\ barite\ weight} \times 100 \qquad (6.1)$$

The solubility test was carried out using varied concentrations of the DTPA ranged from 10% wt to 40% wt to get the optimum concentration. The DTPA concentrations were prepared by diluting the 40% wt using deionized water. The pH of the DTPA solutions was 11.5. Also analytical equipment such SEM (scanning electron microscope) can be used to determine the solubility results of the barite filter cake solids.

Then the effect of adding one of the converting agents selected from the group of potassium carbonate, potassium chloride, potassium formate, potassium nitrate, ammonium carbonate, calcium chloride, magnesium chloride, and sodium carbonate on the dissolution rate of barite in DTPA was evaluated. The effect of the converting agents on barite

dissolution was measured using variable concentrations of these agents to obtain the optimum type and concentration. To investigate the effect of the other drilling fluid solids on the barite dissolution, the dissolution rate of the solids collected from de-sanders during well flow back in DTPA along with the converting agent was measured.

Compatibility of Enzymes in DTPA

Various enzymes were added to the optimum concentration of DTPA to study their compatibilities with DTPA at (200°F). Two concentration of the enzymes were used; 7% wt and 10% wt. The enzymes were added to the DTPA and mixed for 24 hrs. After that the solution was placed in a see through cell at 200°F. Any precipitate from the solution will indicate the incompatibility of the solution. From solubility perspective, the dissolution rate of barite was measured in the presence of the compatible enzyme with DTPA.

Preparation of the Formulation

The concentration and amount of different components used in the developed formulation are listed in Table 5. The original concentration of the enzyme was 100 wt.% and the concentration of DTPA was 40% wt. The barite filter cake removal formulation consists of 20% wt DTPA, 6% wt converting agents, and 7% wt enzyme. Deionized water was used to prepare the required concentration of these components. For example to prepare 100 gm of the removal formulation, the following table explains the required weight for each component.

Table 5 Preparation of the removal formulation

Component	Original concentration, wt.%	Concentration in the removal formulation, wt.%	Required weight, gm
DTPA	40	20 wt.%	50 gm
Catalyst/converter	100	6 wt.%	6 gm
Enzyme	100	7 wt.%	7 gm
		Deionized water	37 gm
		Total weight	100 gm

These weights were calculated using the mass balance as follows, $C_1W_1 = C_2W_2$. The required weight (W_1 = ?) required to prepare 100 gm of the final solution (W_2 = 100 gm) with target concentration 20 wt.% of DTPA (C_2 = 20 wt.%) that has an original concentration of 40 wt.% (C_1 = 40%) can be calculated as follows:

$$W_1 = \frac{C_2W_2}{C_1} = \frac{20\times100}{40} = 50\ gm \text{ of DTPA}$$

The weight of the catalyst required to prepare 6% wt concentration can be calculated as follows:

$$C_1W_1 = C_2W_2 \Rightarrow W_1 = \frac{C_2W_2}{C_1} = \frac{6\times100}{100} = 6\ gm \text{ of catalyst}$$

Finally, the weight of the enzyme required to prepare 7% wt concentration can be calculated as follows:

$$C_1W_1 = C_2W_2 \Rightarrow W_1 = \frac{C_2W_2}{C_1} = \frac{7\times100}{100} = 7\ gm \text{ of enzyme}$$

The rest is the weight of the water (100 gm – 50 gm DTPA – 6 gm catalyst – 7 gm enzyme = 37 gm of water).

We found out that there is no effect of changing the order of mixing these chemicals. The DTAP can be added first and then the catalyst followed by enzyme or DTPA then enzyme followed by catalyst. The most important thing is to keep the mixture mixing for adequate time until form uniform mixture.

HPHT filter cake removal

HPHT static fluid loss test was conducted at 300 psi differential pressure and at 270°F to form the filter cake using actual barite weighted water based mud collected from the field. The filter cake was formed on ceramic disc using 500 ml cell. The thickness of the formed filter cake was measured using computed tomography scan (CT scan) technique. The Ceramic disk (filter medium) was scanned first and then with the filter cake. Digitizing software was used to determine the filter cake thickness.

The developed formulation consists of DTPA, converting agent, and enzyme that were used to study the filter cake removal fluid efficiency. Two types of tests were used to evaluate the efficiency of the designed removal formulation. The first test was solubility test. After the HPHT fluid loss test the formed barite filter cake was removed from the cell and dried in the oven to remove the water. The barite filter cake solid was then used in the solubility test to evaluate the efficiency of the filter cake removal formulation. The solubility of the solids (from the barite filter cake) was measured by adding 4 gm of the filter cake solids to 100 ml of solution in Teflon cell. The Teflon cell placed in aging cell in hot rolling oven for 24 hours at 270°F and 300 psi.

The second test was HPHT removal test. The formed filter cake was placed in HPHT cell with the developed formulation for 24 hour soaking time at 270°F and 300 psi differential

pressure. The weight of filter cake before and after the removal process was recorded to determine the filter cake removal efficiency.

Removal Efficiency Evaluation

To test the efficiency of the removal formulation, a barite filter cake was prepared from a real barite-weighted water-base drilling fluid with the formulation listed in Table 3. The preparation of the barite filter cake was conducted in a standard high temperature high pressure cell (HTHP cell), and the temperature was set at 270°F and the differential pressure set at 300 psi, similar to the temperature (about 250–270°F) and pressure condition under which the drilling fluid is typically used. Ceramic disk was used as the filter media with the cell filled with the barite-weighted drilling fluid. Before the HPHT fluid loss test was conducted the ceramic disk was saturated by water and the weight was recorded for the dry and the saturated disk. Following the weighting of the barite filter cake, the barite filter cake removing formulation was added to the HTHP cell at a ratio of 25 ml of the formulation/g of the filter cake. The cell was again pressurized to 300 psi and heated to 270°F. After 24 hours soaking time, the filter cake removing formulation broke through the filter cake, and any remaining formulation was removed from the cell.

6.3 Characterization and Analysis

6.3.1 Scanning Electron Microscope (SEM)

The chemical composition of the industrial barite was determined using Scanning Electron Microscope (SEM-EDS) to determine the chemical composition of the solids used in this

study (such as industrial barite grade, solids collected from de-sanders during well flow back, and filter cake solids). A JEOL JSM-646LV SEM was used in this study. The samples were dried for at least 6 hours and then gold-coated to be viewed using the SEM's specimens. Similarly, the composition of the solids remaining after the removal process was evaluated to study the change in the chemical composition during the solubility and removal test. The surface area structure of the industrial barite was estimated according the high resolution SEM pictures.

6.3.2 Particle Size Analysis

The particle size distribution of the industrial barite solids was measured using the Wet Dispersion Unit ANALYSETTE 22 Nano Tec plus.

6.4 Results and Discussion

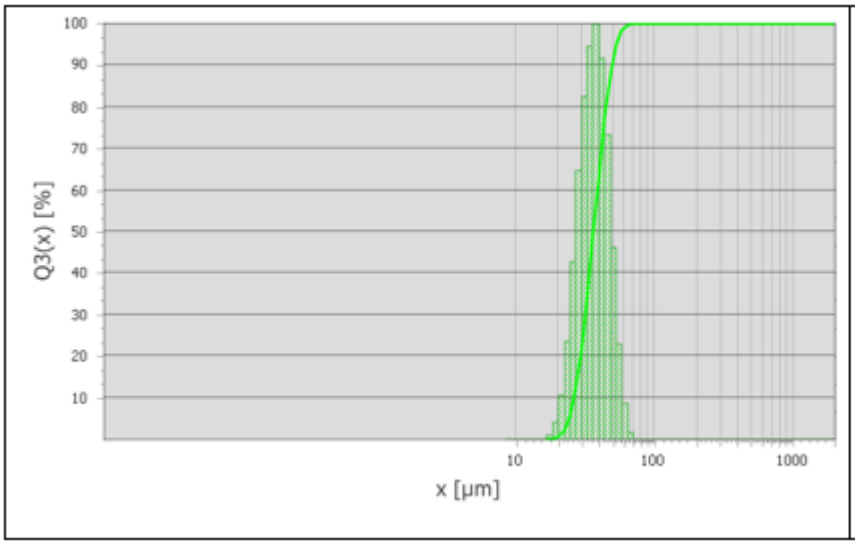
6.4.1 Solids Analysis

The composition of the industrial barite (barium sulphate), the solids collected from de-sanders during drilling, and the filter cake solids used in this work are shown in Table 6. Table 6 shows a comparison between the solids composition obtained by SEM technique. More than one site of the solid samples was tested to have representative data of the composition. The total impurities in the barite sample such as Si, Ca, Fe, Al, and K as shown by EDS data in Table 6 ranged from 6 to 8% wt and the rest of Ba, S, and O formed the barium sulphate. The concentration of the Ba in the filter cake solids composition and

the drilled solids (collected after de-sander) decreased while the impurities such as Si, Ca, Fe, Al, Mg and others increased. The source of these impurities is either from the minerals of the drilled formation (Si, Mg, Al, and Fe) or from the drilling fluid additives (Ca, Na, Cl) such as $CaCO_3$ and NaCl. The particle size results of the industrial barite used in this study is shown in Figure 34. The majority of the particles were in the range of 30 to 45 micron.

Table 6 The composition of the solids used in this study

Industrial Barite			**Solids Collected from De-Sanders during Well Flow Back**			**Filter Cake Solids**		
Element	Spectrum 1	Spectrum 2	Element	Spectrum 1	Spectrum 2	Element	Spectrum 1	Spectrum 2
	Wt.%	Wt.%		Wt.%	Wt.%		Wt.%	Wt.%
Ba	57.39	54.83	Ba	42.15	40.54	Ba	38.75	40.78
O	25.04	27.79	O	34.04	37.24	O	34.15	33.94
S	11.94	11.58	S	10.87	10.60	S	8.52	9.39
Si	3.35	3.63	Si	6.70	5.98	Si	2.81	2.63
Ca	0.48	0.40	Ca	1.87	1.54	Ca	4.33	4.06
Fe	0.56	0.55	Fe	1.86	1.47	Fe	2.91	1.17
Al	0.94	0.89	Al	1.12	1.47	Al	1.41	1.20
K	0.30	0.33	K	0.34	0.33	K	0.39	0.30
			Mg	1.04	0.72	Mg	2.07	1.96
			Zn		0.07	Na	2.99	2.94
			Co		0.05	Cl	1.68	1.61
Total:	100.00	100.00		100.00	100.00		100.00	100.00



Q3(x) [%]	x [µm]
5	23.8
10	**25.9**
25	30.2
50	**36.1**
75	42.7
90	**49**
95	52.5
99	60.2

Figure 34 Particle distribution of barite particles

6.4.2 Solubility and Compatibility

The solubility results showed that the optimum concentration of the DTPA for both potassium and sodium bases was 20% wt, as shown in Figure 35. Increasing the concentration more than 20% wt the reaction will increase at the beginning and this will increase the viscosity and retard the reaction [48]. The results showed that the dissolution capacity of the potassium base DTPA was higher than the sodium base. The maximum dissolution capacity of the 20% wt DTPA potassium base was 67% wt (equals 26.8 g/l) in 24 hours at 200 °F. While the dissolution rate of sodium base DTPA was 38% wt (equals 15 g/l) as a maximum value for the same soaking time (24 hours) and 200°F. The experimental results showed that decreasing the pH of the DTPA solution lower than 11 caused significant reduction of the barite solubility. Decreasing the pH of the 20% wt K_5-DTPA from 11 to 9, the solubility of the industrial barite decreased from 67 to 30% wt. Therefore, based on the experimental results of this work the pH of the DTPA should be more than 11 to achieve higher barite dissolution.

The rate of the dissolution of Ba^{2+} from $BaSO_4$ using chelating agents is affected by several resistances based on the concentration of the chelating agent and the pH of the solution [47]. At low pH, where the chelating agent exists in the acid form, the presence of Hydrogen ions compact the chelating agent and minimize the dissolution of Ba^{2+}. The chelating ability increased by increasing the pH and reaches the maximum for fully deprotonated chelating agent. In our case, at high pH, higher than 11, the dissolution is affected by the concentration of DTPA in the solution. At low concentration of DTPA, lower than 15 wt. %, the driving force between the bulk concentration of DTPA in solution and to that on the surface of barite is low. Therefore, the rate of dissolution is mainly

controlled by mass transport of DTPA. However, at high concentrations, this effect is negligible compared to the effect of the adsorption of DTPA on the surface of barite and solution complexation reaction thereafter. Therefore, the DTPA is first adsorbed on to the surface followed by solution complexation reaction between DTPA and $BaSO_4$.

Different converting agents were added to the K_5-DTPA to improve the solubility of barite and increase the removal efficiency. The results showed that adding some of these agents such as potassium carbonate, potassium chloride, potassium formate to the DTPA increased the solubility of the barite. On the other hand, the presence of ammonium carbonate, calcium chloride, potassium nitrate, magnesium chloride, and sodium carbonate impaired the solubility of barite in DTPA. In particular, the optimum concentration of the converting agent such as potassium carbonate, potassium chloride, potassium formate that should be added to the DTPA was found to be 6% wt. Figure 36 shows that the dissolution rate increased from 67% to 86% by adding 6% wt of K_2CO_3 to the 20% wt K_5-DTPA solution for 24 hours soaking time at 200 °F. The results of this figure also presents the effect of the temperature, where the Figure 36 shows the dissolution rate of barite at 200 °F and 270 °F in the presence of the converting agent and without. Increasing the temperature of the removal formulation will be an advantage of using this formulation to remove the barite filter cake. The high temperature solubility experiments were conducted using Teflon liner cell.

The compatibility of the 20% wt K_5-DTPA with different enzymes (Enzyme A, B, C) was tested at high temperature, 200 °F. The results clearly showed that Enzyme B was not compatible with the DTPA potassium base as shown in Figure 37. Immediately there was a clear separation between the DTPA and Enzyme B was observed. Enzyme C formed a

compatible solution with the DTPA. There was no separation after mixing 10% wt of Enzyme C with 20% wt DTPA and the solution remained stable as function of time. However, Enzyme A also performed compatible solution with DTPA, it was observed that the solution was not stable with time. After 1 hour of mixing, suspended particles in solution were observed as an indication of unstable solution. Although the compatibility results was enough to exclude the two types of these enzymes because of their incompatibility with DTPA, the effect of these three enzymes on barite dissolution rate in DTPA was examined. The results showed that enzyme B has inverse impact on barite dissolution, the solubility of barite decreased from 67% wt to 25% wt by adding only 7% wt to the solution. Whereas adding 7 to 10% wt of the other two enzymes to the solution did not affect the barite dissolution rate in K_5-DTPA. Therefore, the removal process can be conducted in one stage. This is because the enzyme C was compatible with the DTPA and enzyme C did not affect the dissolution capacity of barite in DTPA.

A removal formulation contains 20% wt K_5-DTPA (pH 11.5), 6% wt potassium carbonate, and enzyme C with two concentrations, 7% wt and 10% wt was prepared. The efficiency of the prepared formulation was examined by conducting solubility test using solids collected from de-sanders during drilling (drilling fluid solids). The maximum solubility of the drilling fluid solids in the barite filter cake removing fluid was 78% wt at 24 hrs soaking time and 200 °F equivalent to 31 grams of the solids per litre of the barite filter cake removing fluid. Increasing the temperature to 270 °F the solubility of the drilling solids reached 86% wt. The formulation that consists of enzyme C with 7% wt showed a slightly superiority (2 to 3% wt increment) in solubility value compared with the formulation containing 10% wt. Lowering the concentration of the enzyme to 4% wt

decreased the solubility to 70% wt. Based on that, we decided to go with the 7% wt as an optimum concentration for enzyme C. Therefore, the concentration of the enzyme in the filter cake removal process in this work was kept at 7% wt because it showed the highest efficiency in breaking the polymer in the filter cake.

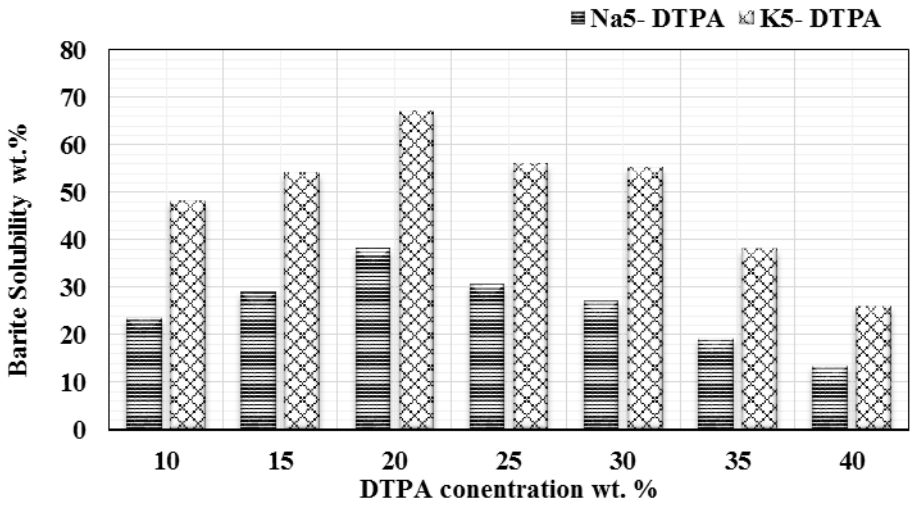


Figure 35 Comparing barite solubility in DTPA potassium and sodium bases (pH 11, 200°F, and 24 hrs)

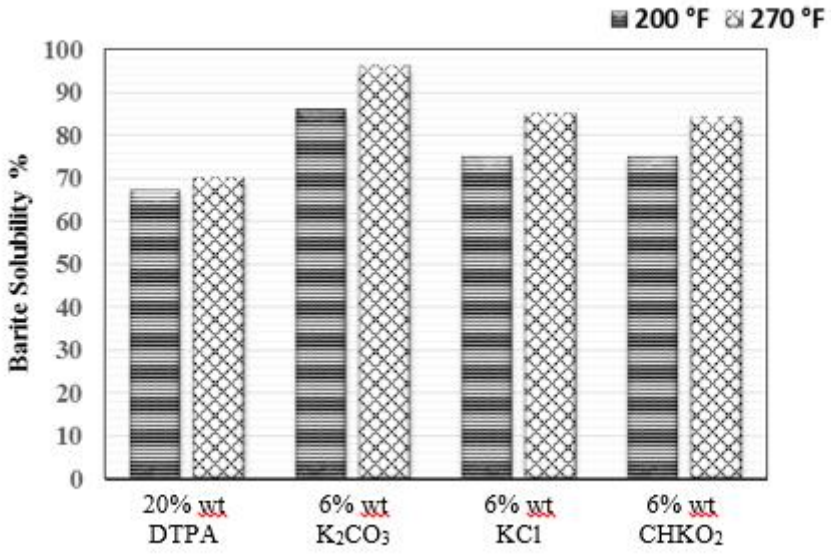


Figure 36 Comparing the barite solubility in 20% wt k_5-DTPA solution alone and with k_5-DTPA plus different (converting/ catalyzing agent; potassium carbonate K_2CO_3, potassium chloride KCl, potassium formate $CHKO_2$) at 24 hours. pH 11.5 at different temperatures (200 °F and 270 °F)

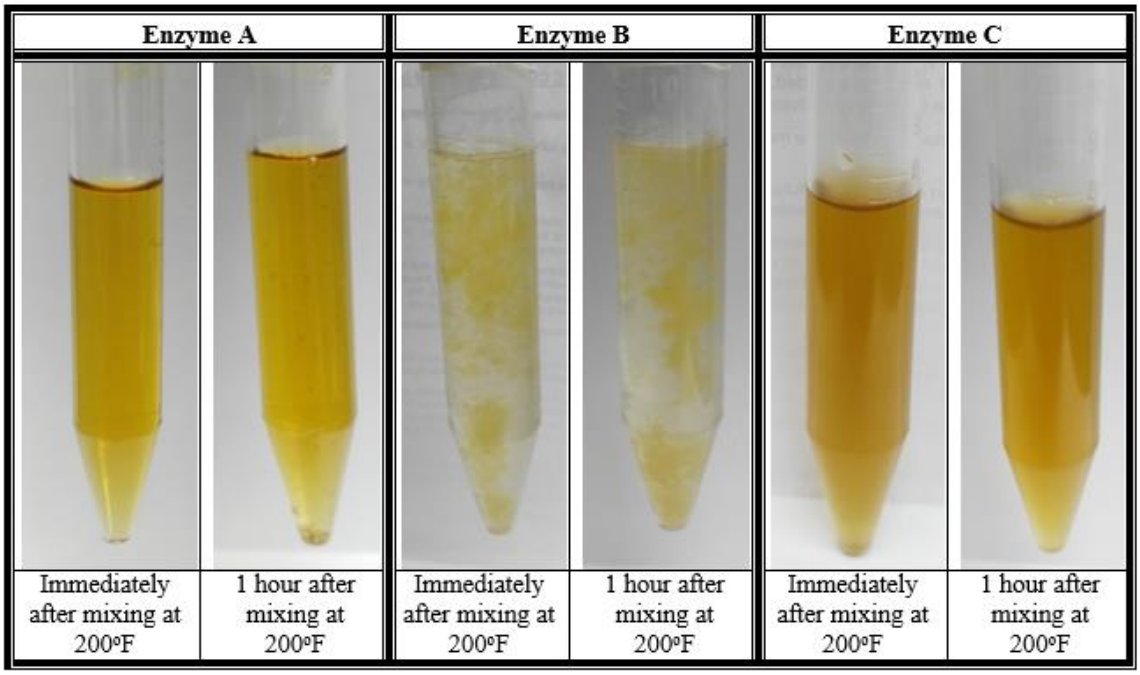


Figure 37 Compatibility of different enzymes with 20% wt DTPA-K_5

6.4.3 Filter cake removal

According to solubility and compatibility tests, the removal formulation consists of (a) polymer removal agent selected from the group consisting a polymer degrading enzyme (enzyme C), (b) high pH chelating agent potassium base DTPA, and (c) at least one converting agent selected from the group consisting of potassium carbonate, potassium formate, and potassium chloride. The formulation consists of 20% wt K_5-DTPA (pH 11.5), 6% wt potassium carbonate and 7% wt of enzyme C.

The filter cake formed as shown in Figure 38 was weighed by a digital balance. At the end of the cake building time, the cell was cooled down and the pressure was released. The remaining fluid was drained from the cell, and the formed filter cake was placed again in the HPHT cell. The treated filter cake was examined visually as shown in Figure 39 and by measuring the weight after the removal process. Compared with the weight of the filter cake before the treatment shown in Figure 38, 90% wt of the filter cake was dissolved by the developed formulation.

The original filter cake thickness before the removal was 1.3 mm, after the removal the remaining filter cake thickness was 0.12 mm. The thickness of the filter cake was obtained by CT scan as explained in section 2.24. The net of filter cake solids was 15.95 gm before the removal. We used the same ratio of the solubility test (4 gm solids in 100 ml removal fluid); 400 ml of the filter cake removal fluid was added to the HPHT cell. The remaining weight of the filter cake solids in the cell after 24 hours was 1.43 gm which indicates that the removal efficiency reached 90%. XRD analysis of the remaining solids after the removal is 100% barite.

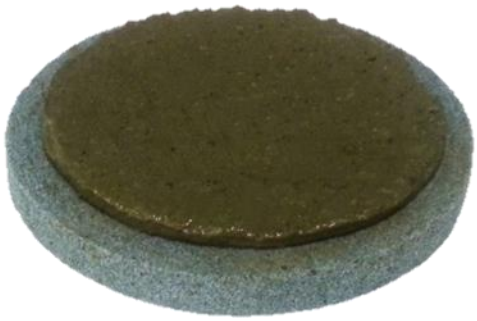


Figure 38 Barite filter cake formed with the barite weighted water based drilling fluid

Figure 39 The removal of the barite filter cake by the barite filter cake removing formulation

From the environmental perspective, filter cake removal with chelating agent based systems (GLDA, EDTA, DTPA, etc.) have been used as an alternative to the conventional acid-based systems such as hydrochloric acid (HCl) to reduce the toxicity, lower the impact on the environment, and minimize the operational challenges [70,79]. Unlike the conventional treatment (HCl), using the investigated removal formulation (DTPA) in the field reduced the environmental and personnel safety risks in term of preparation the solution in the surface and pumping to the well at elevated temperatures. The barite filter cake removal offered less corrosion potential and there is no need to use corrosion inhibitors. Moreover, the enzymes used in the filter cake breakers are inherently environmentally friendly [69]. Mahmoud et al., (2015) [80] stated another environmental advantage of designed barite filter cake removal by DTPA and converting agent that the DTPA is not producing Hydrogen sulfide H_2S gas while it contacts with iron sulfide scale deposited over the face of the tubulars.

Economically, the introduced formulation for barite filter cake removal is cost effective because it can be used in single stage and this will save the pumping and rig time. The current practice is to pump the enzyme first to remove the polymer coating for 24 hrs, then pump the removal formulation, and soak it for another 24 hrs. Using single stage filter cake removal fluid developed in this study will save the pumping time and rig cost. The cost saving will base on the drilling location and daily drilling rate of the drilling rig. In offshore operations the cost saving will be higher compared to the onshore drilling operations.

6.4.4 Pore Hole Volume (PHV) Required in Filter Cake Removal

The thickness of the formed filter cake down hole and the amount of the removal formulation pumped to the well are the main parameters that control the filter cake removal process. The designed formulation as shown in Figure 36 dissolved 86% to 95% of barite equivalent to 35 to 38 grams of the industrial barite solids per liter of the removal formulation at 200 to 270°F. Therefore, to assure higher filer cake removal efficiency (above 85%), each liter of the designed removing formulation must correspond to 35 grams of filter cake solids down hole as the maximum capacity of the designed formulation to dissolve.

The weight of filter cake down hole can be calculated based on the filter cake thickness. The volume of the pumped removal formulation is limited with the open hole diameter. In this study, we developed a new dimensionless number that can be used to design the volume of the required fluid to remove the filter cake. This new dimensionless number is called “Pore Hole Volume”. The term “Pore Hole Volume (PHV)” is defined to link the volume required to dissolve the filter cake effectively with the volume of the open hole section which containing the filter cake. For the hole section shown in Figure 40 assuming that the filter cake has a uniform thickness around the entire hole section, the weight of the filter cake can be calculated as follows:

$$W_{fc} = V_{fc} \times \rho_{fc} = \frac{\pi}{4} L \left[\left(d_h^2 - \left(d_h - 2th_f\right)^2\right] \times \rho_{fc} \qquad (6.2)$$

The volume of the open hole (or the solvent) can be calculated as follows:

$$V_{fl} = \frac{\pi}{4} L \left(d_h - t_{hf}\right)^2 \qquad (6.3)$$

Where:

W_{fc} = weight of filter cake solids, gm

V_{fc} = the volume of filter cake, cc

ρ_{fc} = density of filter cake solids, gm/cc

L = the length of the hole, cm

d_h = the diameter of the open hole, cm

t_{hf} = the thickness of the filter cake, cm

The ratio of the filter cake solids to the removal fluid volume can be calculated by dividing **Eq (6.2)** by **Eq (6.3)**. So, if this ratio is greater than 35 gm/ liter (the maximum capacity of the designed formulation to dissolve) that means the volume required to dissolve the down hole filter cake is greater than the open hole section volume. In contrast, if this ratio is lower than the maximum capacity of the designed formulation to dissolve, that means the required volume to dissolve the down hole filter cake is less than the volume of the open hole section. Thus the term"Pore Hole Volume (PHV)" to dissolve the filter cake effectively can be determined by dividing **Eq (6.4)** by the maximum capacity of the designed removal formulation (35 gm/liter).

$$W_R = \frac{d_h^2 - \left(d_h - 2th_f\right)^2 \times \rho_{fc}}{\left(d_h - 2th_f\right)^2} \qquad (6.4)$$

$$PHV = \frac{W_R}{maximum\ capability\ of\ the\ designed\ formulation\ to\ dissolve} = \frac{W_R}{35} \qquad (6.5)$$

Where; W_R is the ratio of the filter cake solids to the removal fluid volume, and this is required for the solubility test. For example if this ratio is 0.1 it means we need 10 ml fluid to remove 1 gm of the filter cake solids.

Equation 6.**5** does not consider the effect of the filter cake porosity. The filter cake porosity was found to be in the range of 10% to 30% (Ba geri et al., 2015a). So, by introducing the filter cake porosity term $\emptyset_c$ to equation (6.5) in the calculation of filter cake solids weight, the number of PHV can be given as follows:

$$PHV = \frac{W_R\,(1-\emptyset_c)}{maximum\ capability\ of\ the\ designed\ formulation\ to\ dissolve} = \frac{W_R\,(1-\emptyset_c)}{35} \quad (6.6)$$

The number of Pore Hole Volume (PHV) required to dissolve the barite filter cake effectively using barite filter cake removal fluid investigated by this work is shown in Figure 41 as function of the barite filter cake thickness for different open hole diameters. Figure 41 data obtained using equation 5 assuming that the worst case where the porosity of the filter cake was zero. It is clear that injecting one PHV of the barite filter cake removal fluid for 24 hrs soaking time is sufficient to efficiently remove barite filter cake with thickness of 2 mm, 1.5 mm, and 1.3 mm for hole diameter of 12 1/4, 9 5/8, and 7 5/8 inch respectively as shown in Figure 41. That means if the horizontal section length is 1000 ft, the volume of one PHV is 2370 gallons for the 7 5/8 inch open-hole diameter. The cost of preparing one gallon of barite filter cake removal about 7 USD including the cost of DTPA, the converting agent, and enzyme. Thus treating 1000 ft of horizontal section may ultimately cost about 16,000 USD of the barite filter cake removal.

In our case, for a gas well with (9 5/8) inch hole and a filter cake thickness of 1.3 mm, the number of Pore Hole Volume (PHV)" required to dissolve the barite filter cake effectively (e. g. with removal efficiency higher than 90%) equal to 0.85 of the open hole section, as referred to Figure 41. In this case, pumping one pore hole volume of the removal formulation will be enough to remove the filter cake effectively. The only concern is the cases where the formed filter is thick and the required volume is more than one PHV(filter cake thickness equals to 2 mm). One PHV of the removal fluid should be pumped and soaked with the filter cake for 24 hours and then circulating the remaining of the required volume. The barite filter cake solids density was assumed to be 3.5 gm/cc close the barite density 4.2 gm/cc and with considering the presence of some other elements in the filter cake solids that have lower density value which make the overall filter cake density less than the barite density (see the filter cake composition shown in Table 6**.**

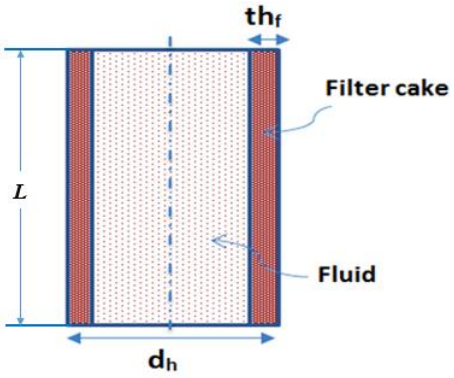


Figure 40 A diagram illustrating the filter cake on the wall of the formation

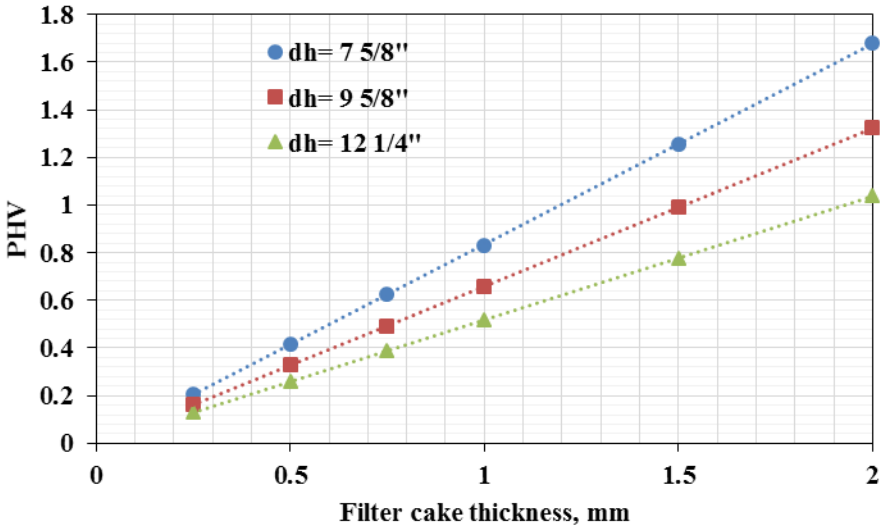


Figure 41 Number of Pore Hole Volume (PHV)" required to dissolve the filter cake effectively. dh is the open hole diameter

6.5 Summary

Based on the results obtained from this study to develop barite filter cake removal formulation; the following conclusions can be drawn:

- In this study, we developed a formulation that can effectively remove the barite filter cake from deep oil and gas wells during drilling operations. The developed formulation consists of 20% wt potassium base DTPA chelating agent, 6% wt converting agent (such as potassium carbonate), and 7% wt enzyme to degrade the polymer. This formulation can be used to remove the barite filter cake in single stage.
- The barite filter cake removal efficiency reached 90% at 270^{o}F and 24 hrs soaking time.
- High pH DTPA potassium base (K_5-DTPA) with a concentration 20% wt provided the maximum barite dissolution rate. The solubility of barite in K_5-DTPA reached to 67% at 24 hrs and 200°F (equal to 26.8 g/l) and it reached 70% as the temperature increased up to 270°F. Using the sodium base (Na_5-DTPA) decreased the barite solubility to 38% wt (equal to 15 g/l) as the maximum value.
- Adding one of the following converting agents; potassium carbonate, potassium formate, and potassium chloride with 6% wt concentration to the 20% wt K_5-DTPA solution increased the barite solubility up to 86%, 75% and 75%, respectively, for 24 hrs soaking time at 200°F. By increasing the temperature to 270°F, the barite solubility reached 96%, 85% and 85% in presence of potassium carbonate, potassium formate, and potassium chloride with 6% wt concentration, respectively.

- Enzyme # C was compatible and stable with K_5-DTPA and it did not affect the barite solubility.
- An equation to determine the number of Pore Hole Volume (PHV) required to pump down hole to remove the barite filter cake effectively was developed based on the result of this study.
- The developed formulation does not require corrosion inhibitors because it is high pH and this will minimize the environmental impact.
- The single stage filter cake removal by the developed formulation will save the rig cost compared to the currently used multi-stage filter cake treatment.

CHAPTER 7

Removal of Barite (Barium Sulfate BaSO4) Scale

Barite scale is one of the significant issues facing the oil and gas industry due to the low solubility of barite in Hydrochloric (HCl) and other acids. Chelating agents such as DTPA (Diethylene Triamine Pent acetic Acid), EDTA (Ethylene Diamine Tetra Acetic Acid), and HEDTA (Hydroxy Ethylene Diamine Tri Acetic Acid) were introduced as barite scale removers but the solubility of barite in these chemicals was very low. Huge amount of chelating agents are required to remove the barite scale but we are constrained by the hole volume of the well.

In this chapter, a novel formulation was developed to dissolve the barite scale by using chelating agents and a catalyst to enhance the solubility of barite in chelating agent (DTPA) with small volume of chelating agents. Using the catalyst in this formulation is the main feature of the treatment. Solubility experiments were conducted to determine the dissolution rate of barite in the (DTPA) at high temperatures (200 °F). The effect of pH on the dissolution rate of barite was studied using two bases (potassium base KOH and Sodium base NaOH). The optimum chelating agent (DTPA) concentration and time was identified that will achieve the maximum barite scale solubility. Also, the optimum catalyst type and concentration was determined using the high temperature solubility experiments.

7.1 Introduction

Barite (barium sulfate) is a common weighting agent used in the oil and gas industry due to its high density. Mainly the barite is used as a weighting material in the drilling /completion fluids to drill/complete deep oil/ gas wells to control high formation pressure. The invasion of the mud filtrate due to the pressure difference will create mud cake that mainly composed of barite; also some of the barite solid particles will invade to the formation causing barite scale that might reduce the reservoir permeability in the near-wellbore. During production operations, the barite particles will be produced with oil/ gas and formed barite scale around the casing and production tubing and also they will cause erosion to the surface chokes and surface valves [81].

Another cause of barite scale formation is attributed to the use of sea water with high sulfate content in injection operations where in the water zone abundance of barium ions are there. The barium sulfate scale is formed due to the incompatibility between the sea water (high sulfate content) and the reservoir water (high barium content) [43,44].

From the removal point of view, barium sulfate scale is hard to remove due to the very low solubility of barium sulfate in the water (2.3 mg of barite /Liter of water) ($Ksp = -10^{-9.99}$ at 25°C) [77]. Also the barite is not soluble in Hydrochloric (HCl) and other acids [40]; that make this problem more complicated to be solved by ordinary chemicals. Therefore, the cost of production operations increased due to changing the well tubular or using mechanical operations to remove the barite scale.

As mentioned earlier, the barite scale is not soluble in HCl, so there is a massive need to develop a new formulation that can dissolve the barite scale. As an alternative to acid-based

systems, the chelating agents have been widely used for different applications such as enhanced oil recovery (EOR) fluids in carbonate and sandstone reservoirs [82–85]. Chelating agents were used as an effective solution to remove the scale formed in the electrical submersible pump (ESP) during the production [86]. Environmentally friendly chelating agents are believed to have limited impact which made them good applicant to be used a scale removal from sensitive down hole equipments such as ESP. Chelating agents also were used to prevent and inhibit calcium sulfate scale during sea water injection[87]. Also the corrosion problems of the well tubulars associated with using high aggressive acid treatments such HCl motivate us to develop a new formulation using chelating agents due to their low corrosive nature. Several chelating agents were found to be environmentally friendly, readily biodegradable, and gentle to the well tubulars [82].

Different chelating agents were evaluated to dissolve the barite scales in the oil and gas industry operations [37–39]. Mostly, special attention was paid to DTPA and EDTA [77][45][88][89]. Lakatos et al. [37] evaluated the dissolution rate of barite particles in seven different chelating agents; (DTPA, EDTA, HEDTA, DOCTA, NTA, DCTA and TTHA) at 25 °C. They found that DTPA (concentration 0.1 mole/litter) proved to be the best dissolver for barite. The dissolution capacity of DTPA (0.1 mole/litter) was 8 kg of barite in cubic meter of solution (equal to 8 grams per litter) at 25°C for 5 days contact time. The capacity of EDTA (0.1 mole/litter) was around 5g/litter at the same conditions. The chelating agents were prepared by the NaOH in their study. For this reason, this study focuses on enhancing the utilization of DTPA to remove the barite scale with adding catalysts that increase the dissolution of barite in DTPA. Also we changed the base of DTPA from sodium base Na-DTPA to potassium base K-DTPA to enhance the solubility

of barite scale.

Using the potassium base (potassium hydroxide KOH) to prepare the DTPA solution, Putnis et al. [45] conducted experimental work to study the dissolution process of barium sulfate by a DTPA solvent. The aqueous solution of DTPA solvent was prepared by dissolving DTPA using 1.5M solution of KOH to prepare a 0.05M to 0.5M concentration of the DTPA where the pH was kept in the range of 11 to 12 [45]. They studied the dissolution process of barite in DTPA as function of time by different DTPA concentration in the temperature range of 23°C to 100°C using 1 gm of Barite in 100 ml of the solvent. Based on their results, at low temperature (23°C) the concentration of DTPA solution played an important role in the dissolution rate of barium sulfate at low time period (less than 50hr). The results showed that about 80% of barite (equal to 0.8 gm in 100ml based on their set up solid to solvent ration; 1 gm in 100ml) can be dissolved suing DTPA concentrations ranged from 0.05M to 0.25M. Increasing the temperature up to 100^{o}C, the solubility of barite increased sharply up 80 to 85% in 2 hours using DTPA concentrations of 0.25 0.125 and 0.05 M. the increment of barite dissolution wan trivial (up to 90% maximum equal to 0.9 gm of barite in 100 ml of DTPA solvent) by increasing the time up to 4 hours.

A major concern using DTPA to dissolve the barite scale, the capacity of DTPA dissolution (9 gm of barite per liter of DTPA ranged from 0.05M to.25 M) [39] will not be sufficient to dissolve larger amounts of barite scale.

All previous studies did not consider the limitation of the volume constraint in the well or the formation during their studies. Barite needs a lot of DTPA volume to be completely

removed, but we cannot achieve this in oil and gas wells because we are constrained with the hole size. Based on extensive literature survey the objectives of the current paper are to; (1) calculate the volume to weight ratio that can be used for barite removal from oil and gas wells; (2) develop a formulation to dissolve the barite (barium sulfate) scale with high dissolution capacity using DTPA (Diethylene Triamine Penta acetic Acid) and catalysts, (3) determine the optimum concentration and type of DTPA and catalyst at high temperature that will achieve the maximum barite dissolution capacity, and (4) study the effect of different factors on the dissolution rate such as contact time and pH to obtain the optimum time and pH to dissolve the barite scale.

7.2 Solids-to-Liquid Ratio Measurements

For the unit length, the scale weight (W_{sc}) in Figure 42 equals to

$$Wsc = \frac{\pi}{4}(Td^2 - Fd^2)\,\rho_{sc} \quad \textbf{(}8.1\textbf{)}$$

The fluid capacity of the tubing where the scale already formed can be determined using the following equation:

$$Vf = \frac{\pi}{4}Fd^2 \quad \textbf{(}8.2\textbf{)}$$

$$\frac{Wsc}{Vf} = \frac{(Td^2 - Fd^2)}{Fd^2}\,\rho_{sc} \quad (8.3)$$

Where: W_{sc} the weight of the scale formed in the tubing, Td inside diameter of tubing before the scale formed, F_d the inside diameter of tubing after the scale formed, ρ_{sc} density of the scale (barite 4 g/cc to 4.2 g/cc), Vf fluid volume in the tubing after the scale formed. If we assume that the inside diameter of tubing diameter is 6 inches before the barite scale formed and the diameter of the tubing reduced 1 mm scale formed around the wall of the tubing; so the Solids-to-Liquid Ration using equation 3 will be 5.3 gm of barite (assuming the barite density 4 g/cc) to 100 ml volume of solvent fluid. Therefore, we can say that the developed formulation to remove the barite scale should gain removal capacity around 40 gm of barite per liter of solvent.

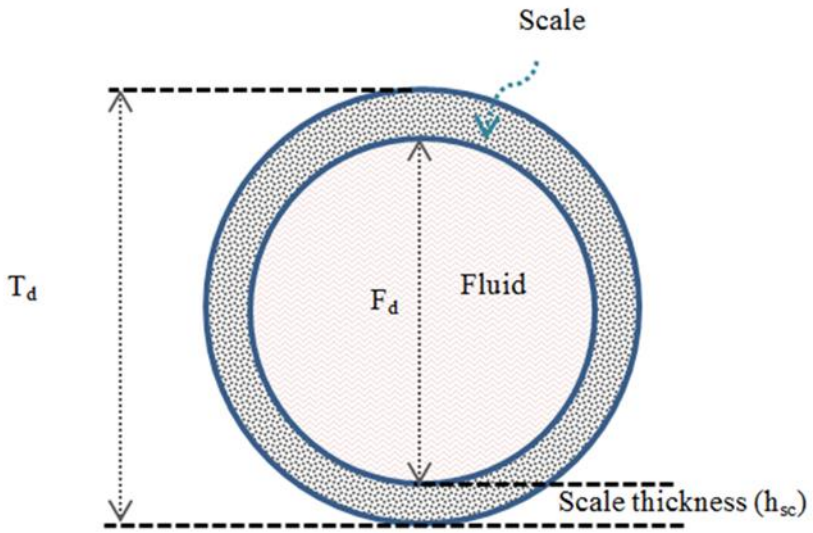


Figure 42 a schematic of scale formed around the wall of the tubular

7.3 Materials and Experimentation

7.3.1 Materials

Pure grade (97 to 100%) barite (barium sulfate $BaSO_4$) was used in this study to evaluate the dissolution rate of barite in the chelation agent DTPA. Two types of DTPA (Diethylene Triamine Penta acetic Acid) were used in this study; the first one was K_5DTPA and the second one was Na_5DTPA. The distilled water was used to make up the DTPA solution in different concentration range. The concentrations used in this study were prepared from and an initial DTPA concentration of 40 wt% liquid.

Different catalyst groups were used in this study such as carbonate group catalysts, chloride group catalysts, formate and other type of catalysts. The idea behind using these types of catalyst is to improve the dissolution rate of barium sulfate (barite) in the DTPA chelating agent. Figure 43 shows molecular structure of the DTPA; the DTPA has five of carboxylate functional groups (ligands) which bind to metal center having different number of nitrogen atoms [39].

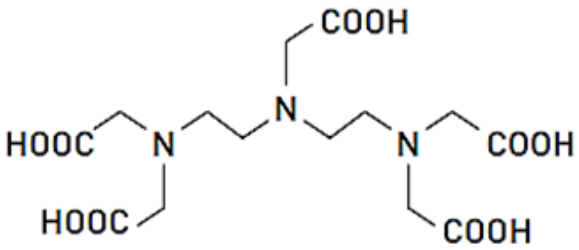


Figure 43 Molecular structure of the DTPA

7.3.2 Experimental Work

Solubility test

Most of the previous dissolution experiments used to measure the solubility has no base to select the ratio of solid weight in (g) to the solvent volume in (ml). For instance, Putnis et al. [39] used 1 g of barite in 100 ml of solvent (DTPA); Nasr-El-Din et al. [40] used 20 g of barite in 250 ml of solvent equal to (8 g/100ml); Lakatos [38] used 5 g of barite in 40 ml of the solvent equivalent to (12.5g/ml). Based on the target of this work is to increase the solubility of barite up about 50 g in litter. The solubility test in this work conducted using 5 g of barite in 100 ml of solvent (DTPA + catalyst). The solution was mixed in flask using constant stirring rate (350 rpm) and the flask was connected to reflux condensers to ensure no water loss by evaporation at high temperature. The experimental carried out using the following procedure to develop the final formulation:

a) Using different concentration of DTPA (sodium and potassium salts) ranged from 10 wt% to 40 wt%. The experimental carried out at 80^{o}C. The time during this stage was kept constant 24 hours and the pH was kept in the range (11 – 12).
b) Select the optimum concentration and type of DTPA from part (a). Determine the dissolution rate of barite using the optimal DTPA concentration (obtained from part **a**) as function of pH value using same experimental condition in part a.
c) Adding different catalysts such as (potassium carbonate K_2CO_3, potassium chloride KCl, potassium formate $CHKO_2$, and others) with varied concentration to determine the optimum catalyst concentration. The experimental was kept same

as in part a (80^{o}C) and the pH as obtained from part b.

d) Using the final formulation (DTPA plus catalyst) to determine the dissolution rate of barite as function of time.

The solubility of the barite was measured by taking the original weight of the barite at the start of the experiment (4 g used in 100 ml) and the weight of the remaining barite (not soluble in the solvent) at the end of the experimental. The difference between these two weights equal to the weight of the dissolved barite in 100 ml of the solvent.

Surface Area and Pore Size Distribution Measurements

Surface area and pore size distribution were obtained using ASAP 2020 Micromerihis. The barite samples were tested before and after treatment with DTPA. Each sample with 0.35 – 0.4 g was first degassed at 300^{o}C for 3 hrs to remove humidity and other volatile materials. Then, it was tested for adsorption/ desorption of N_2 at 77 K. The adsorption/ desorption hysteresis curve, as well as, pore size distribution obtained by Barret- Joyner-Halenda (BJH) Analysis were recorded. This test was carried out to determine impact of DTPA on the pore size distribution of barite particle.

7.4 Results and Discussion

Dissolution of Barite in DTPA

The solubility test of the pure barium sulfate $BaSO_4$ (barite) indicated that the optimum concentration of the Diethylenetriamine penta potassium acetic acid (DTPA-K_5) was 0.5

M as shown in Figure 44. At this concentration of DTPA-K_5 0.5M the dissolution rate of the barite reached its maximum value about 70 wt. % equal to (34 g/l) at 80 °C in 24 hours. The pH of the DTPA-K_5 was kept above 11 using KOH in the case of K_5DTPA or NaOH in the case of Na_5DTPA to achieve the maximum dissolution capacity. Hydrochloric acid (HCl) was used to reduce the pH of DTPA solution to 7. The barite dissolution rate at pH 7 decreased to 20% (10 g/l). Altering the base of the DTPA from the potassium base (DTPA-K_5) to the sodium base (DTPA-Na_5) resulted in the reduction of the solubility to half (35 wt. % equivalent to 16 g/l) at the same test condition; 80 °C in 24 hours.

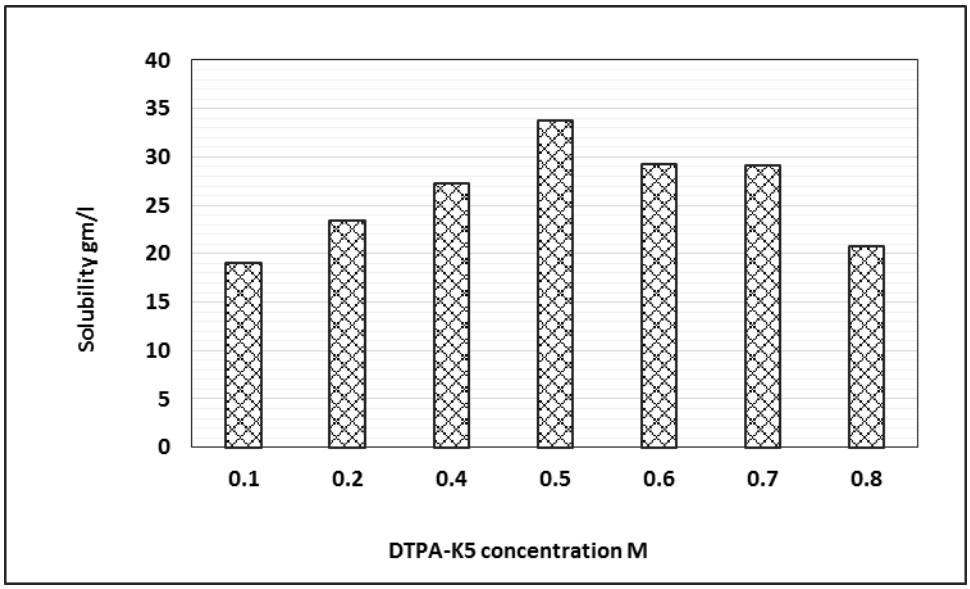


Figure 44 Barite Solubility with K_5-DTPA- Base pH 11 -12 at 80 °C, 24 hr.

Surface Area and Pore Size Distribution

The hysteresis curves for N_2 adsorption/ desorption by barite samples before and after treatment with DTPA-K_5 (0.5 M) are shown in Figure 45. At relative pressure bellow 0.5, both hysteresis curves show similar up late and release of N_2 with an average monolayer capacity of 0.0085 mmol/g. This value has increased to 0.031 mmol/g for the treated sample and to 0.018 for the original one. This indicates more pores were opened during treatment as a result of leading out barite from pores surface leading to open more pores in the sample. Both curves showed type III hysteresis loop indicating the presence of macro-pores in barite surface. This is concluded in incremental pore volume distribution shown in Figure 46 and pore area distribution in Figure 47 where major pore volume exist at average pore width greater than 500 Å. Treatment with DTPA has increased half pore volume from 0.0033 cm^3/g to 0.0065 cm^3/g and increased pore area from 0.3770 m^2/g to 0.6712 m^2/g.

The adsorption average pore width for micro-pores 20.2 Å and 19.5 Å for original and treated sample, respectively. In addition the treated sample demonstrated an increase of mesopores from 314.6 Å to 423.5 Å and a macrospores from 352.5 Å to 390.2 Å which indicates leading out barite from samples pores. This indicates that DTPA chelating agent was able to penetrate inside barite particles and enlarge the pore space and the reaction not only in the surface.

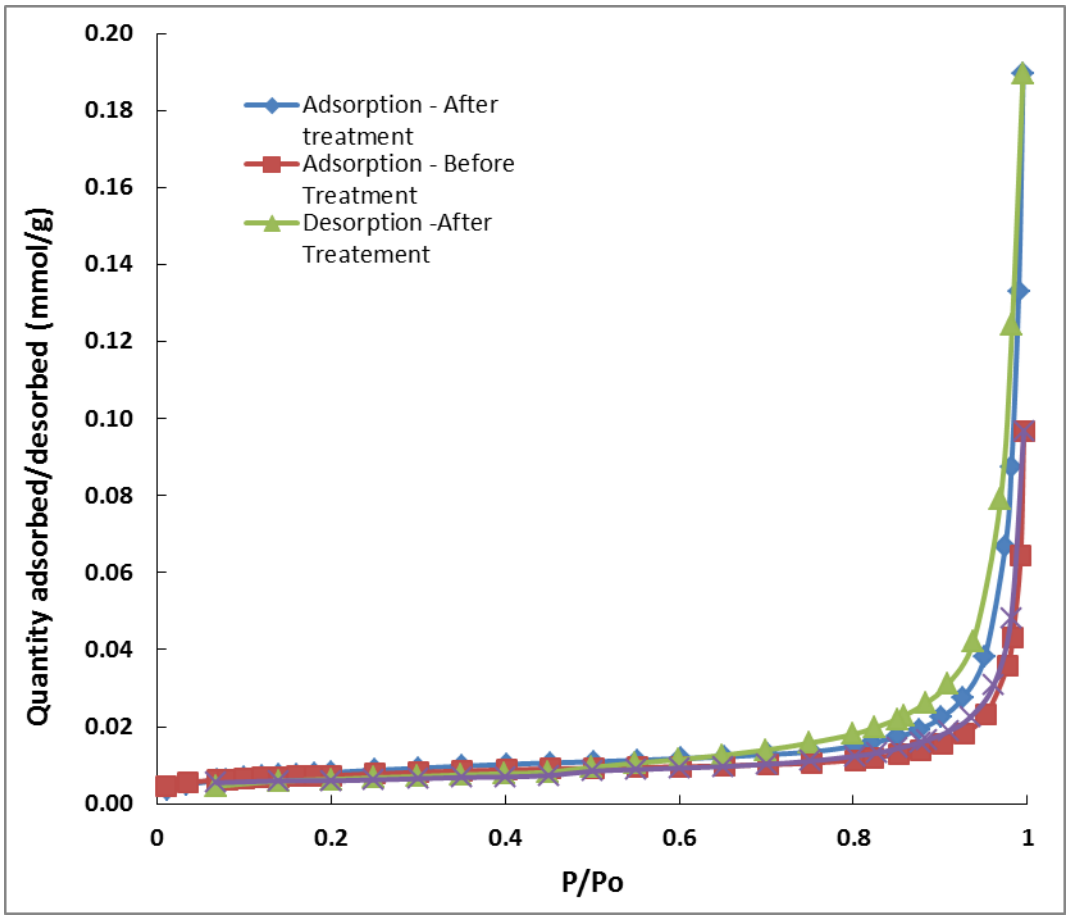


Figure 45 The hysteresis curves for the adsorption/ desorption of nitrogen by Barite samples before and after treated with K_5-DTPA

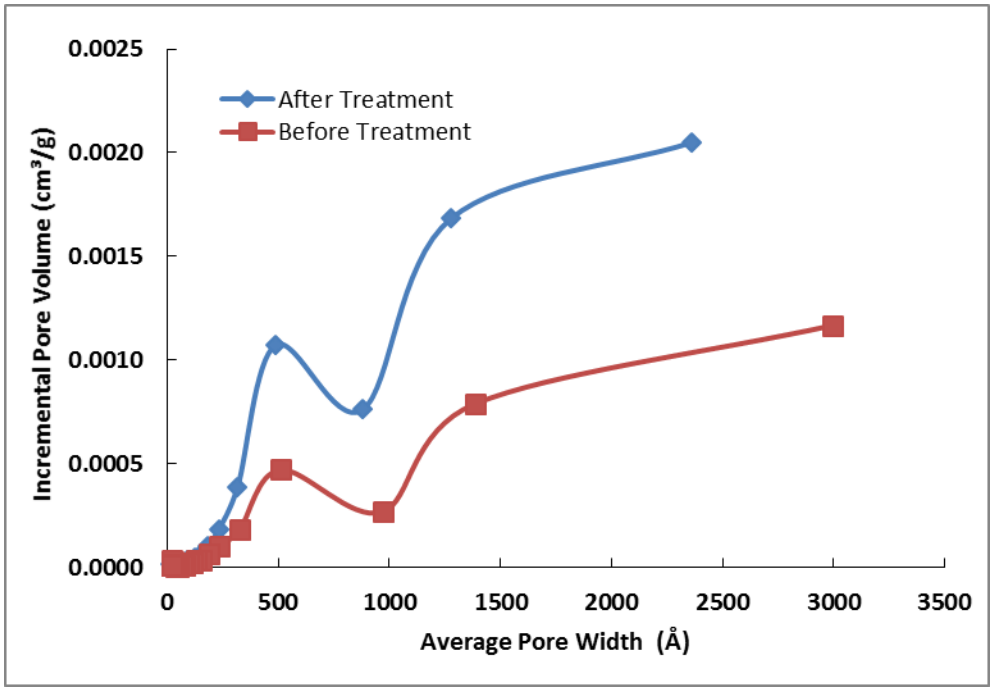


Figure 46 the pore volume incremental distribution of Barite samples before and after treated with K_5-DTPA

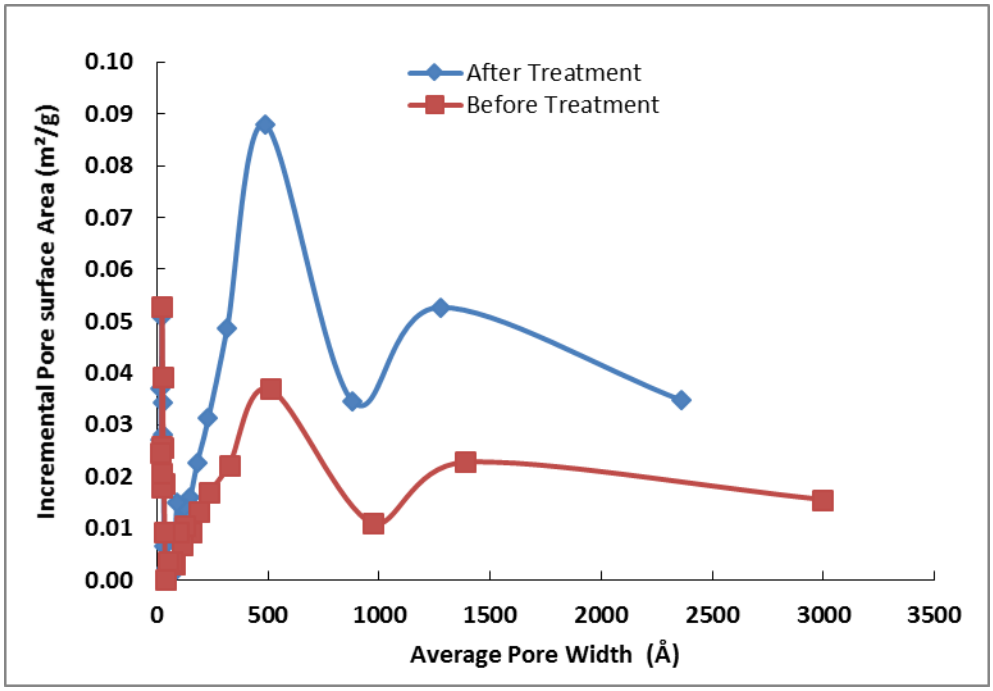


Figure 47 the pore surface area incremental distribution of Barite samples before and after treated with K_5-DTPA

Effect of Converting/ Catalyzing Agent on Barite Dissolution by DTPA

To enhance the solubility of barite in the DTPA-K_5 it was found by this study that at least one of the following converting agents should be selected from the group consisting of potassium carbonate, potassium formate, and potassium chloride. Adding potassium carbonate to the solution (0.5M DTPA-K_5) with a concentration ranged from 5 to 7wt% dissolved the same amount of barite (34g/l) in 4 hours compared to 24 hrs by 0.5M DTPA only without catalytic/converting agents. Accordingly, adding the potassium carbonate converting/catalyzing agent effectively reduced the time for the barite scale removal. The barite removal capacity of the solution containing 0.5M DTPA-K_5 and 5 to 7wt% potassium carbonate increased by 25% (from 70% to 95%) in the same time (24 hours). Figure 48 shows the increment of the barite solubility caused by adding potassium carbonate as converting/catalyzing agent. In the presence of the potassium carbonate in the DTPA solution another important observation obtained from Fig 7, the dissolution capacity of the barite reached 85 wt% in 6 hours, whereas for the extended 18 hours only 10 wt. % increment of the barite dissolution. The observed effect of using the converting/catalyzing agents becomes more dominant on the time scale. In such situation, for high thick barite scale we can double the treatment fluid volume in 12 hours which will achieve more barite scale removal in shorter time.

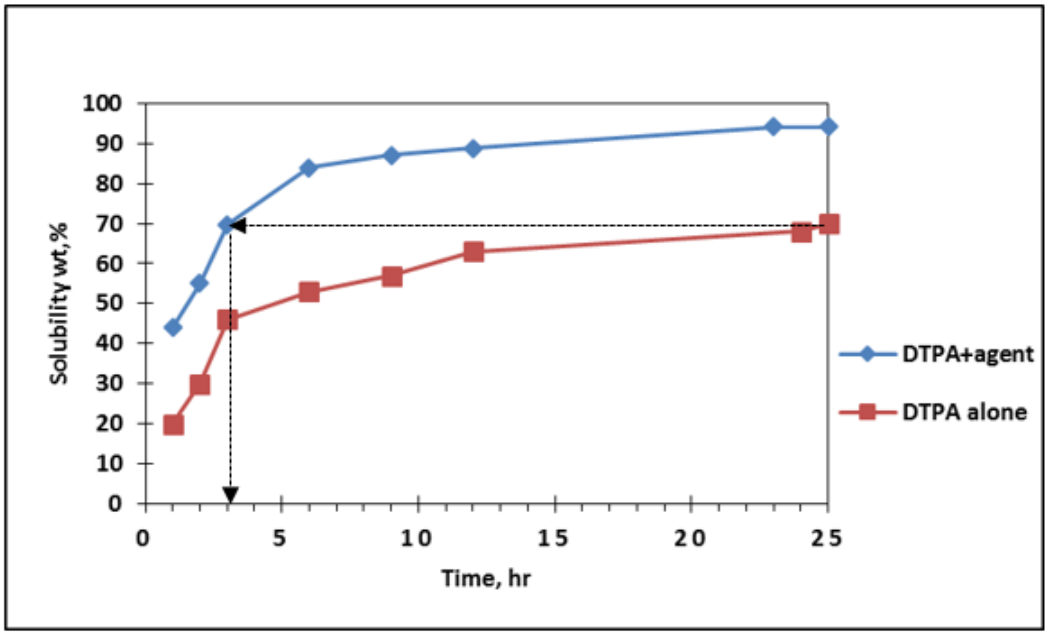


Figure 48 comparing the barite solubility in DTPA solution with DTPA plus potassium carbonate (converting/ catalyzing agent) as function of time. pH 11 -12 at 80 °C

The other converting/catalyzing agents result is shown in Figure 49. This figure compares the barite solubility in 0.5M DTPA solution alone with 0.5M DTPA in addition to different catalysts/converters such as potassium carbonate K_2CO_3, potassium formate $CHKO_2$, and potassium chloride KCl) at 6 and 24 hours. The converting agents were tested at different concentrations varied from 1 to 10 wt%. The barite solubility enhanced greatly after adding the converting agents and it is most likely that the optimum concentration of these agents ranged from 5 to 7 wt% with respect to pH 11 -12 at 80 °C. The agents added to the DTPA solution are capable of increasing the dissolved amount of barite in 6 hours more than that in 24 hours using the DTPA-K_5 alone, as shown in Figure 49.

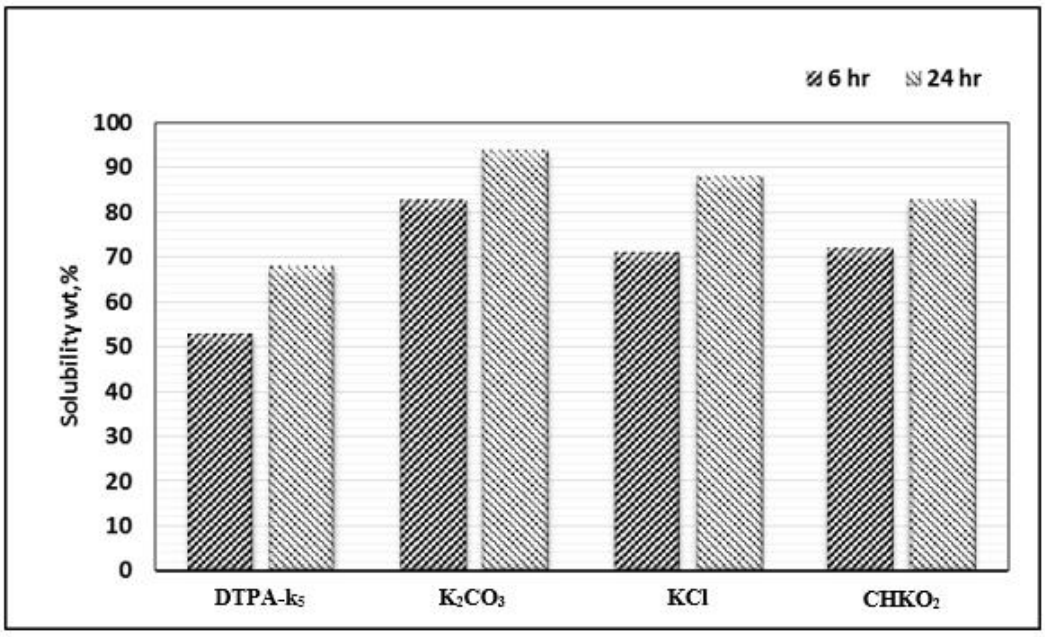


Figure 49 comparing the barite solubility in DTPA solution with DTPA plus different (converting/ catalyzing agent; potassium carbonate K_2CO_3, potassium formate $CHKO_2$, potassium chloride KCl) at 6 and 24 hours. pH 11 -12 at 80 °C

7.5 Summary

In this chapter, a new effective formulation to dissolve the barite scale is presented. The following are the conclusions that were drawn from this study:

- DTPA chelating agents based on potassium yielded higher solubility compared to DTPA based on sodium.
- The optimum concentration of DTPA that gave the highest barite solubility was 0.5M and the pH should be more than 11 to obtain high solubility.
- Adding catalysts/converters to DTPA enhanced the solubility of barite in DTPA nd 95% solubility was achieved by adding different catalysts.
- DTPA chelating agents reacted with barite particles at the surface and inside the particles as shown in the pore size distribution before and after treatment with barite.

CHAPTER 8

REACTION OF DTPA WITH BARITE USING RDA AND SURFACE AREA DISTRIBUTION IN PRESENCE OF CATALYST

In this part, the mechansium of the reaction between DTPA and barite lonely and within the presence of the catalyst was studied used the Rotating Disk Apparatus (RDA) and Surface Area and Pore Size Distribution Measurements.

8.1 Materials and Experimental

8.1.1 Materials

Industrial barite grade powders (75 micron) were used for the solubility test. Barite (barium sulfate) core samples used to carry out the Rotating Disk experimental were obtained from Mawad Drilling Company. Disks with a thickness of 1 inch and 1 inch diameter were cut form the barite block, Figure 50. The surface of the disks were highly polished to be ready for using in Rotating Disk Apparatus. The purity of the samples were determined using XRD and SEM. The porosity of each disk was measured.

Diethylenetriaminepentaacetic (DTPA) acid used in this study. The molecular structure shows that DTPA has a five of carboxylate functional groups (ligands) which bind to metal centre having three of nitrogen atoms [39,40].. At high pH the ligand forms strong 1:1

chelates in solution. Based on that the ligand can be either Na or K based on the used base to prepare the solution; in our study KOH was used to prepare the solution. The reason of using potassium base DTPA was explained earlier in chapter 5 and 6. At high pH condition, DTPA became progressively deprotonated and the affinity for barium ions increased. Therefore, the pH the DTPA solution was kept above 12.

Different catalyst groups were used in this study such as carbonate group catalysts, chloride group catalysts, formate and other type of catalysts. The idea behind using these types of catalyst is to select the optimum catalyst type and concentration the increase the dissolution rate of barium sulfate (barite) in the DTPA chelating agent.

Figure 50 Barite disks for rotating disk experimental

8.1.2 Material Characterization

The chemical composition of the industrial barite was determined using Scanning Electron Microscope (SEM-EDS) to evaluate the purity of barite before the dissolution with the chelating agent. Similarly, the composition of the solids remaining after the dissolution was evaluated to study the change of the chemical composition during the solubility test. The surface area structure of the barite was estimated according the high resolution SEM pictures before and after the dissolution with chelating agent. The samples were dried for at least 6 hours and then gold-coated to be viewed using the SEM's specimens.

X-ray diffraction spectroscopy was used to measure the mineralogy of the industrial barite (using with PANalytical X-ray, Philips Analytical). The XRD data was used as a confirmation for the EDS analysis results. The XRD also was carried out to determine the mineralogy of the solids precipitated at the end of the solubility test.

Surface area and pore size distribution were obtained using ASAP 2020 Micromerihis. The barite samples were tested before and after treatment with DTPA lonely and within the presence of catalyst. Each sample with 0.35 – 0.4 g was first degassed at 300^{o}C for 3 hrs to remove humidity and other volatile materials. Then, it was tested for adsorption/ desorption of N_2 at 77 K. The adsorption/ desorption hysteresis curve, as well as, pore size distribution obtained by Barret- Joyner- Halenda (BJH) Analysis were recorded. This test was carried out to determine impact of DTPA on the pore size distribution of barite particle.

8.1.3 Experimental Work

The solubility experiment was carried out using 4 gm of barite solids in 100 ml of the DTPA. This ratio was obtained to simulate the downhole filter cake Solids-to-Liquid Ratio based on thickness of the formed cake and the diameter of the wellbore as well as the porosity of filter cake [7]. Variable concentrations of DTPA (ranged from 10 to 40 wt. %) were used to pick up the optimum concentration with respect to the maximum barite dissolution rate. The solubility test carried out at (190° to 200°F) for constant time (24 hours). Based on the previous step, the optimum concentration was designated with respect to the maximum barite dissolution. After that, to investigate the optimum type and concentration of the catalyst/converting agents on the barite solubility, different catalysts such as (potassium carbonate K_2CO_3, potassium chloride KCl, potassium formate $CHKO_2$, and others) with varied concentration were added to the solution.

The Rotating Disk Apparatus was used to study the reaction rate of barite in DTPA. The main parts of the Rotating Disk Apparatus are the fluid reservoir, reaction vessel and the auto sampling part as shown Figure 51. The system is associated with gas booster system connected to nitrogen cylinder to control the pressure. The experimental was conducted at high temperature 250 °F and high pressure 1000 psi. Heat-shrink Teflon tubing was using to mount the barite disk on a spindle using so that only the face of the barite disk was exposed to DTPA. The fluid is heated in the reservoir and then transported to the reactor vessel. The concentration of DTPA was 20 wt. % and the pH was kept at 11.5. The reaction kinetics of DTPA with Barite were conducted at four rotational speeds 500, 1000, 1500, and 2000 rev/ min.

Figure 51 Rotating Disk Apparatus

8.2 Results and Discussion

8.2.1 Characterization Analysis

The purity of the barite samples was measured by X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) analysis. The morphological analysis of the samples surface was conducted using scanning electron microscopy (SEM). The elemental analysis by SEM-EDS analysis for the barite samples was conducted in different Spectrum to cover variable sites of the same sample. Based on EDS data, the impurities including (Si, Al, Ca and others) was ranged from 5% to 7 wt% in average of all Spectrums as shown in Figure 52. Although the EDS result showed that the purity of the barite is around 94%; the peaks appeared by the XRD analysis at 20.46 2θ (011), 22.79 2θ (111), 24.87 2θ (002), 25.86 2θ (210), 26.85 2θ (102), 28.75 2θ (211), 31.53 2θ (112), 32.81 2θ (020), 42.59 2θ (113) and 42.93 2θ (122) considered that the purity of the barite as 99-100 wt% with some unknown peaks represented the impurities. the morphological analysis by SEM (5μ) scale high resolution picture displayed that the size of the pores in the barite particles The pore size of the barite particles was found to be around 2-3μ in length and 1-2μ width.

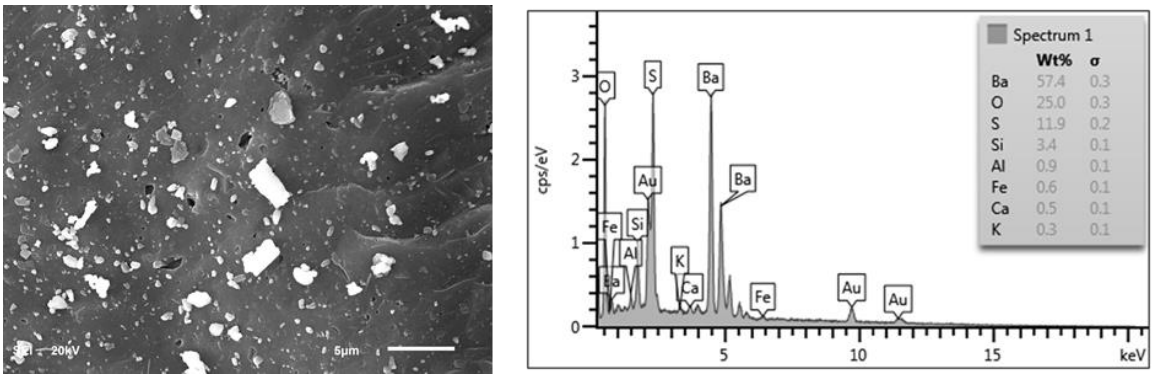


Figure 52 Elemental analysis of the Barite solids using SEM and EDS

8.2.2 Solubility Analysis

The result of solubility test shows that the 20 wt% concentration of potassium salt DTPA-K_5 yielded the maximum dissolution rate of barite particles at high pH (11.5 - 12). The dissolution capacity of the Barite in DTPA potassium base is shown in Figure 53. In particular, the dot plot corresponding to the right y-axis in Figure 53 shows that the maximum removal capacity was about 67 wt.%. This means that 26.8 grams of industrial barite was dissolved per liter of 20 wt. % DTPA-K_5, as shown by the bar graph corresponding to the left y- axis of Figure 53. In contrast, the solubility results showed that using sodium salt DTPA-Na_5 is not recommended to dissolve the barite. The experimental results showed that about the maximum barite solubility in DTPA-Na_5 was 38 wt% (15 g/L).

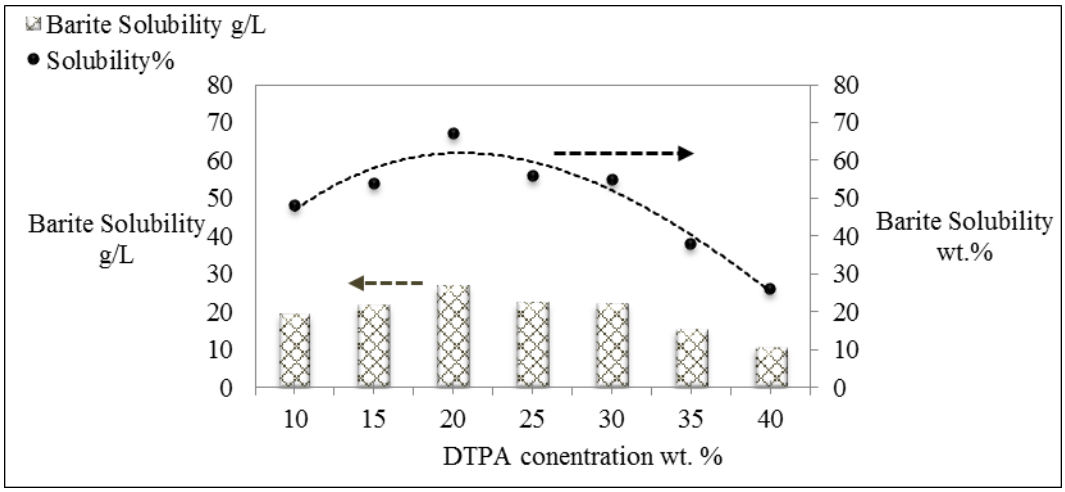


Figure 53 Barite Solubility with DTPA- Potassium Base pH (11.5 -12) at (190°-200 °F), 24 hr.

To enhance the solubility of barite in the DTPA-K_5 it was found by this study that at least one of the following converting agents should be selected from the group consisting of potassium carbonate, cesium chloride, potassium formate, and potassium chloride. Adding potassium carbonate to the solution (20 wt.% DTPA-K_5) with a concentration ranged from 5 to 7wt% increased the barite solubility by 27% from about 67% to 95% (26.8 g/L to 35 g/L) in the same time (24 hours). In the presence of the catalytic/converting agents the solubility of barite reach to 70 wt% in 4 hours only whereas the same amount of barite dissolved in 24 in DTPA alone. The phenomena about the effect of the catalytic/converting agents on the diffusion coefficient will be discussed in the following sections.

8.2.3 Rotating Disk Apparatus Analysis

Figure 54 shows the photo of the barite disk surface after the reaction with chelating agents which lasted 30 minute. The surface photo demonstrates that the surface reaction highly increased by adding the catalytic/converting agents.

Disk surface before the reaction | Disk surace after reaction with DTPA | Disk surace after reaction with DTPA+Catalyst

Figure 54 Photos of disk surface before and after the reaction with DTPA and DTPA with catalyst, RPM=2000 rev/min, Temperature 120 °C, pressure 1000 psi.

The weight loss analysis of the barite disk was measured as function of the rotational speed of the disk in the reactor after 30 minutes. The weight loss of the barite disk in DTPA and DTPA with catalyst is shown in Figure 55. Four rotational speeds were used 500, 1000, 1500 and 2000 rev per minute were used. The weight loss of the barite disk during the after the reaction was measure using the following equation [90]:

$$W_L = \frac{W_B - W_A}{W_B} \times 100 \qquad (1)$$

Where

W_L : weight loss,

W_B : weight of the barite disk before the reaction,

W_A : weight of the barite disk after the reaction

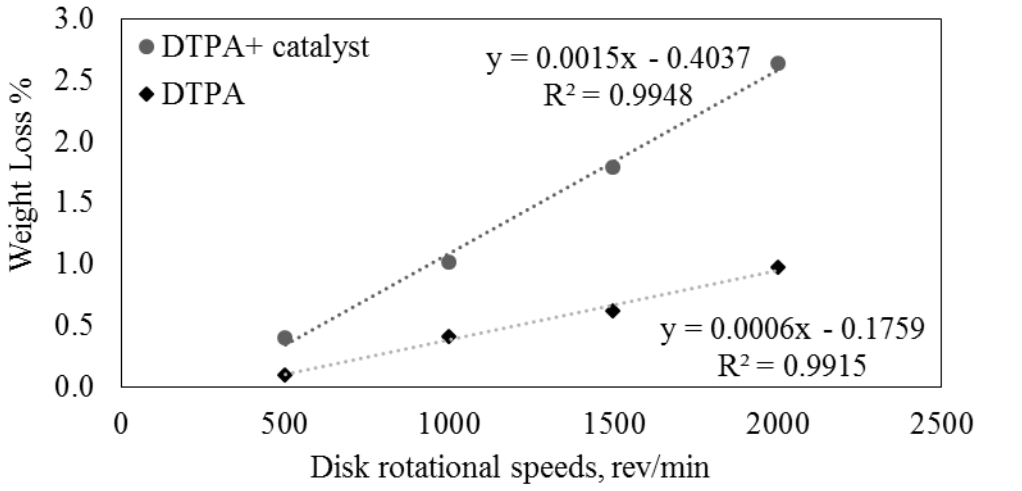


Figure 55 Weight loss of Barite disks after 30 minutes in DTPA alone and DTPA with catalyst at various disk rotational speeds, Temperature 120 °C, Pressure 1000 psi

Reaction Rate analysis: Figure 56 shows the barium ion concentration in mg/L during each RDA experimental as a function time and at various disk rotational speeds. It clear that the dissolution of the barium in DTPA increased as the rotational speed increased.

The rate of the dissolution of Ba^{2+} from $BaSO_4$ using chelating agents is affected by several resistances based on concentration of the chelating agent and the pH of the solution [47]. At low pH, where the chelating agent exists in the acid form, the presence of Hydrogen ions compact the chelating agent and minimize the dissolution of Ba^{2+}. The chelating ability is increased by increasing the pH and reaches the maximum for fully deprotonated chelating agent. In our case, at high pH, higher than 11.5, the dissolution is affected by the concentration of DTPA in the solution. At low concentration of DTPA, lower than 15 wt. %, the driving force between the bulk concentration of DTPA in solution and to that on the surface of barite is low. Therefore, the rate of dissolution is mainly controlled by mass transport of DTPA. However, at high concentrations, this effect is negligible compared to the effect of the adsorption of DTPA on the surface of barite and solution complexation reaction thereafter.

Surface an

8.2.4 Surface Area and Pore Size Distribution

The hysteresis curves for N_2 adsorption/ desorption by barite samples before, after treatment with DTPA-K_5 (alone) and DTPA-K_5 within the presence of the catalyst are shown in Figure 58 and 59. At relative pressure bellow 0.5, both hysteresis curves show similar up late and release of N_2 with an average monolayer capacity of 0.0085 mmol/g.

The adsorption/ desorption for the treated barite with DTPA potassium base in presence of catalyst in the solution reached higher value that adsorption/ desorption for the original one and the barite treated by DTPA alone, Figure 58 and 59. This indicates more pores were opened during treatment as a result of leading out barite from pores surface leading to open more pores in the sample as shown in Figure 60 and 61.Both curves showed type III hysteresis loop indicating the presence of macro-pores in barite surface. This is concluded in incremental pore volume distribution shown in Figure 61 and pore area distribution in Figure 60 where major pore volume exist at average pore width greater than 500 Å.

The presence of the catalyst caused and extract of the barium surface so more barium so the pore and surface are exposed to the chelating agent was increased. This indicates that catalyst/ converting agent was able to penetrate inside barite particles and enlarge the pore space and the reaction not only in the surface. As result of that the distribution of the pores surface area and volume was slightly change after the treatment.

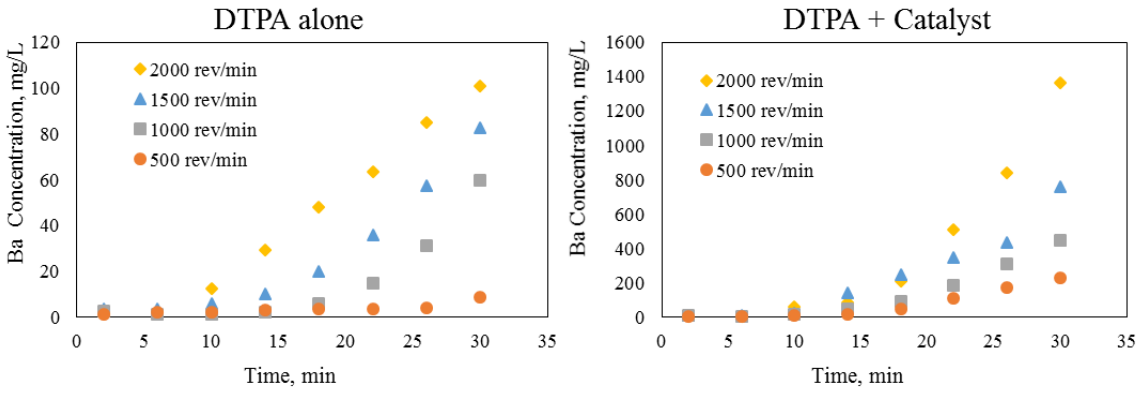


Figure 56 Barium ion concentration as function of disk rotational speeds in DTPA alone and DTPA with catalyst.

Temperature 120 °C, Pressure 1000 psi.

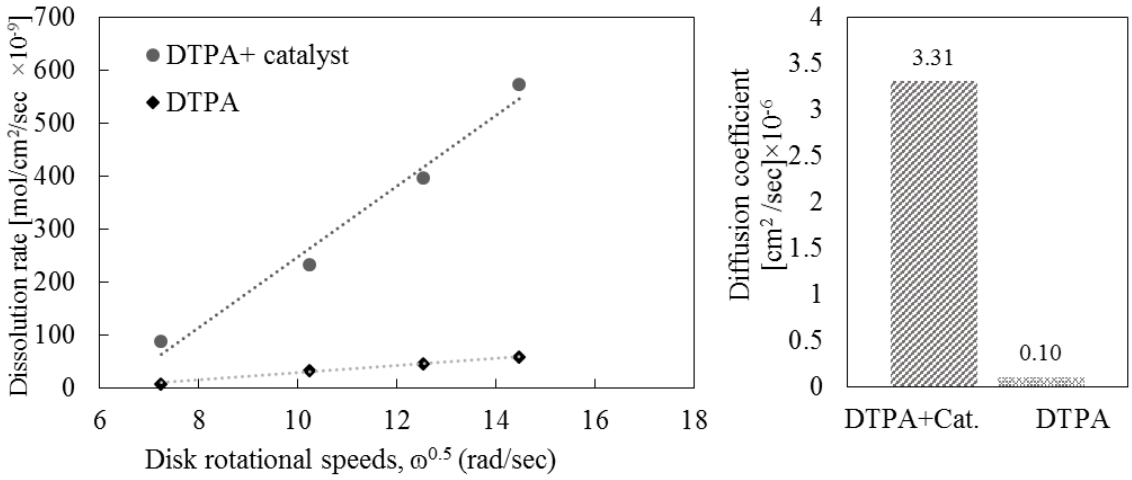


Figure 57 Dissolution rate and Diffusion coefficient of barite in 20 wt.% DTPA and 20 wt. DTPA with catalyst

Temperature 120 °C, Pressure 1000 psi

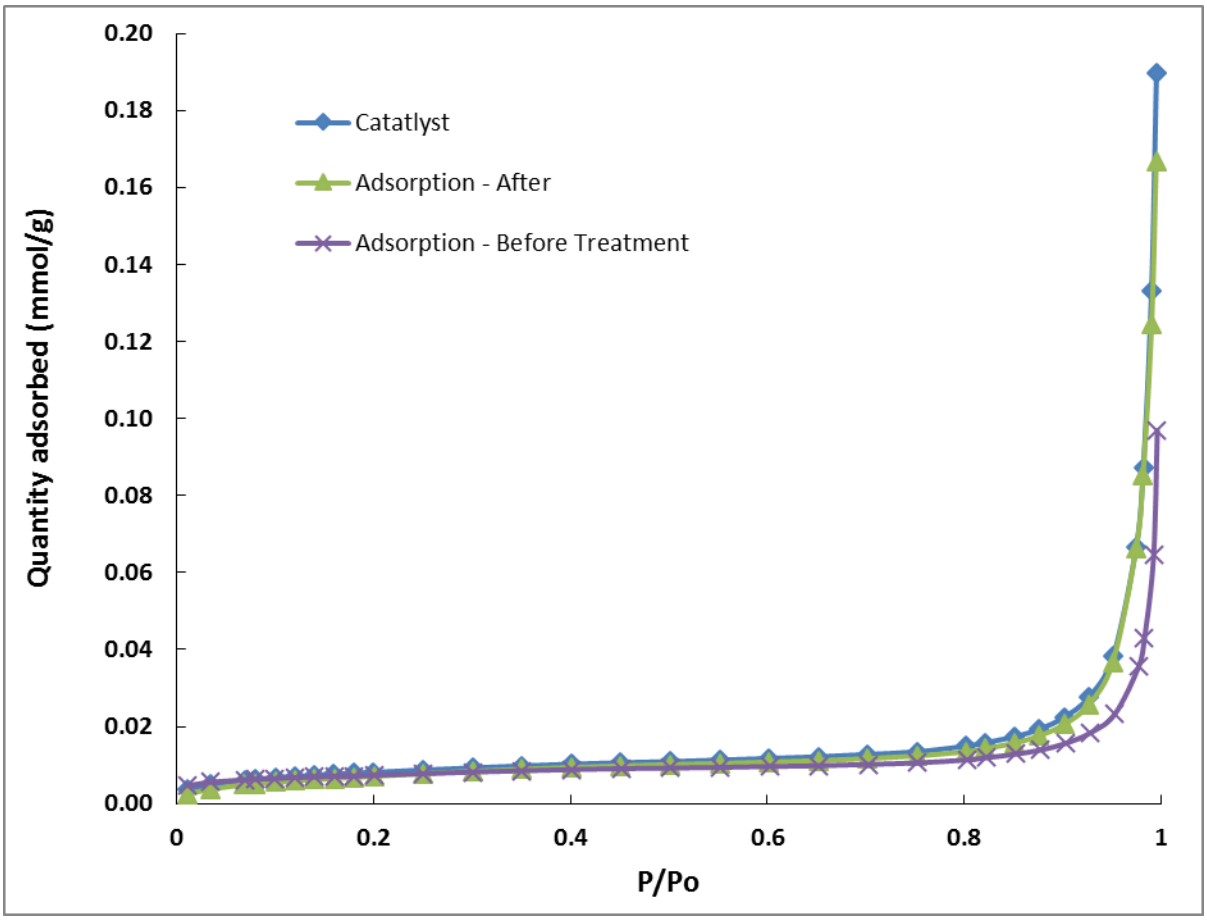


Figure 58 The hysteresis curves for the adsorption of nitrogen by Barite samples before and after treated with K_5-DTPA alone and DTPA-K5 in presence of catalyst

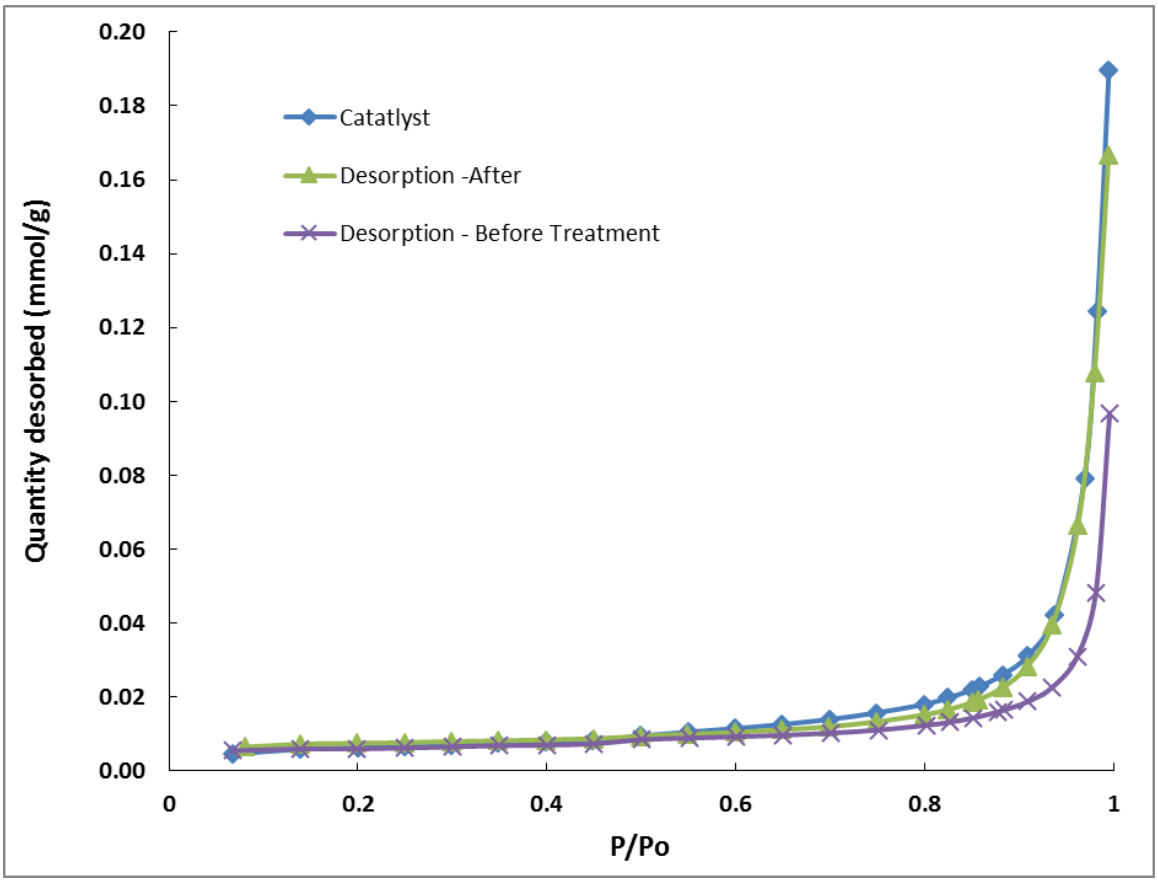


Figure 59 The hysteresis curves for the desorption of nitrogen by Barite samples before and after treated with K_5-DTPA alone and DTPA-K5 in presence of catalyst

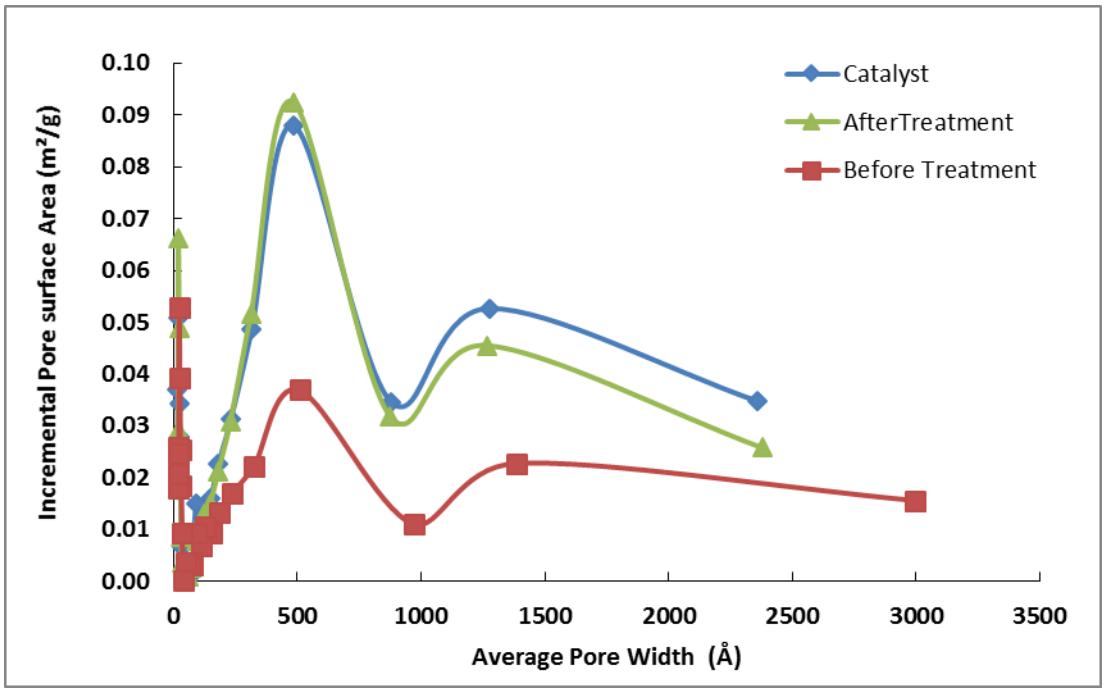


Figure 60 the pore surface area incremental distribution of Barite samples before and after treated with K_5-DTPA alone and DTPA-K5 in presence of catalyst

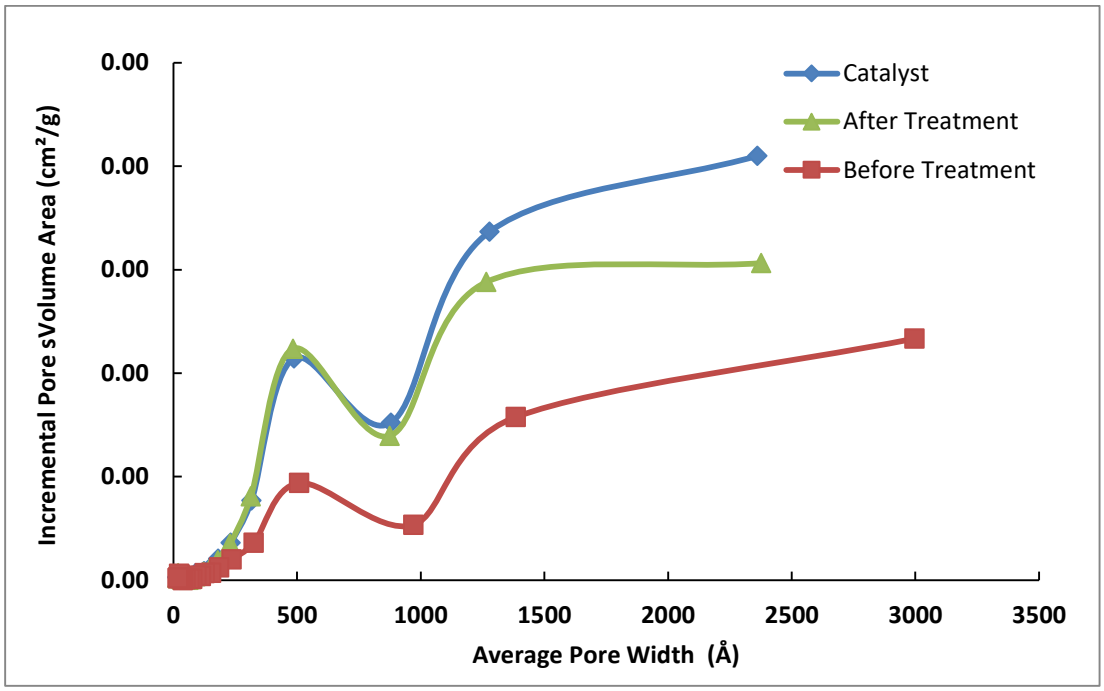


Figure 61 the pore volume incremental distribution of Barite samples before and after treated with K_5-DTPA alone and DTPA-K5 in presence of catalyst

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

Based on the results obtained from this study, the following conclusions can be drawn:

- An innovative formulation that can effectively remove the barite filter cake from deep oil and gas wells was developed.
- The composition of the developed barite filter cake removing formulation is given as: 20% wt potassium base DTPA chelating agent, 6% wt converting agent (such as potassium carbonate), and 7% wt enzyme to degrade the polymer. This formulation can be used to remove the barite filter cake in single stage.
- The barite filter cake removal efficiency reached 90% at 270^{o}F and 24 hrs soaking time.
- High pH DTPA potassium base (K_5-DTPA) with a concentration 20% wt provided the maximum barite dissolution rate. The solubility of barite in K_5-DTPA reached to 67% at 24 hrs and 200°F (equal to 26.8 g/l) and it reached 70% as the temperature increased up to 270°F. Using the sodium base (Na_5-DTPA) decreased the barite solubility to 38% wt (equal to 15 g/l) as the maximum value.
- Adding one of the following converting agents, viz., potassium carbonate, potassium formate, and potassium chloride with 6% wt concentration to the 20% wt K_5-DTPA solution, increased the barite solubility up to 86%, 75% and 75%, respectively, for 24 hrs soaking time at 200°F. By increasing the temperature to

270°F, the barite solubility reached 96%, 85% and 85% in presence of potassium carbonate, potassium formate, and potassium chloride with 6% wt concentration, respectively.

- Enzyme # C was compatible and stable with K_5-DTPA and it did not affect the barite solubility.
- An equation to determine the number of Pore Hole Volumes (PHV) required to pump the mix downhole to remove the barite filter cake effectively was developed based on the result of this study.
- The developed formulation does not require corrosion inhibitors because it has high pH and this will minimize the environmental impact.
- The single stage filter cake removal by the developed formulation will save the rig cost compared to the currently used multi-stage filter cake treatment.
- The developed formulation is also capable to dissolve barium sulphate scale.

9.2 Recommendations

Based on the results and the investigations conducted in this work, we recommended the following:

Selecting the base of the chelating agents has a significant effect on the solubility. Therefore, for any future work a special focus should be on the selection of chelating agent base.

Based on our results, the recommended value of filter cake solids to solvent ratio to be used in future work for testing the filter cake removal is to use 4 gm of filter cake solids in 100 ml of solvent. This recommended ratio approximately represents an average 2 mm filter cake thickness for an open hole of diameter around 9 5/8 inches. The ratio can be re-adjusted using the developed equation in this study.

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Vitae

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PERSONAL

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Nationality	:	Yemeni
Linguistic skills	:	Arabic, and English

EDUCATION

June 2007: B.Sc., Petroleum Engineering with Honor, Hadhramout University of science and technology. [GPA 90.2%]

May 2012: M.Sc., Petroleum Engineering, King Fahd University of Petroleum & Minerals. [GPA 3.75 out of 4]

Master Thesis Topic; Evaluation *of Filter Cake Mineralogy in a Horizontal Well*

September 2012 to November 2016: Ph.D., Petroleum Engineering, King Fahd University of Petroleum & Minerals. [GPA 3.58 out of 4]
Ph.D. Thesis Topic; *Filter Cake Removal of Barite Water-based Mud*

Experience

2010- to Date: Lab Researcher (graduate student), King Fahd University of Petroleum & Minerals.

2009-2010: Teacher Assistant in petroleum department Hadhramout University of science and technology.

2012: Consultant, for three months in EXPEC Advanced Research Center, Formation Damage & Stimulation Unit, SAUDI ARAMCO.

2015: SPE Certified from SPE Formation Damage Workshop, 2015

Specialties:

- Petroleum Engineering
- Filter cake removal
- Filter cake properties
- Scale problems
- Barite and pyrite problems
- Drilling Fluids
- Solid analysis using (SEM, XRD, XRF, FTIR, BET ….etc)
- Reaction Mechanism using RDA

Publications and Participation

1. Patents

1.1. Ba Geri, B. and Mahmoud, M.A. 2016. Zero Invasion Acidic Drilling Fluid. US 20160024370 A1. Application Number: 14/337,310.

1.2. Ba Geri, B., Mahmoud, M.A., Shawabkeh, R.A., and Abdulraheem, A. 2015. Single and Multi-Stage Removal of Barite Scale and Barite Filter Cake. US 450231, Filed.

1.3. Mahmoud, M.A. Ba Geri, B.A., and Ibnelwaleed, A.H., 2015. A New Formulation to Remove Pyrite and Different Types of Iron Sulfide Scale in Oil and Gas Wells. US 449896, Filed.

2. Accepted/Published Journal

2.1. **Ba Geri, B.S.**, Mahmoud, M.A., Al-Mutairi, S.H. and Abdulraheem, A,. **2016**. Effect of Sand Content on the Filter Cake Properties and Removal during Drilling MRC wells in Sandstone Reservoir. *Journal of Energy Resources Technology,* **138** (3), 032901. (Impact factor 2.0, Q2 ranked journal).

2.2. Mahmoud, M.A., **Ba Geri, B.S.,** Elkatatny, S., and Al-Mutairi, S.H., 2016. Modeling of Filter Cake Composition in Maximum Reservoir Contact and Extended Reach Horizontal Wells. Accepted, *Journal of Energy Resources Technology*, JERT-16-1117, Transaction of ASME. (Impact factor 2.0, Q2 ranked journal).

2.3. **Ba Geri, B.S.,** Mahmoud, M.A., Shawabkeh, R.A., and Abdulraheem, A., **2016**. Evaluation of Barium Sulfate (Barite) Solubility Using Different Chelating Agents – Different Bases - at High Temperature. Accepted, *Petroleum Science and Technology, PST-1509-1292.* (Impact factor 0.9, Q3 ranked journal).

2.4. **Ba Geri, B.S.,** Mahmoud, M.A., Abdulraheem, A, Al-Mutairi, S.H. and Shawabkeh, R.A., **2016**. Single Stage Filter Cake Removal of Barite Weighted Water Based Drilling Fluid. Accepted, Journal of Petroleum Science and Engineering, PETROL 7690. (Impact factor 1.7, Q2 ranked journal).

2.5. **Ba Geri, B. S.,** Mahmoud, M. A., and Elkatatny, S., **2016**. Impact of Sand Content on Filter Cake and Invert Emulsion Drilling Fluid Properties in Extended Reach Horizontal Wells. Accepted, *International Journal of Oil, Gas, and Coal Technology, IJOGCT 132764.* (Impact factor 0.7, Q2 ranked journal).

3. Submitted Journals

3.1. Ba Geri, B.S., Mahmoud, M.A., Shawabkeh, R. A., Al-Mutairi, S. H., and Abdulraheem, A ., **2015**. Towards a Complete Removal of Barite (Barium Sulfate $BaSO_4$) Scale Using Chelating Agents and Catalysts. Submitted to the *Arabian Journal of Science and Engineering*, AJSE-D-15-04102.

3.2. Elkatatny, S., Mahmoud, M. A., and **Ba Geri, B.S., 2016**. Evaluation of Using HEDTA Chelating Agent to Clean-Up Long Horizontal Heterogeneous Sandstone Wells without Divergent. Submitted to Journal of Petroleum Exploration and Production Technology, PEPT-D-16-00016.

4. Journals under preparation

4.1. Evaluation the Reaction Mechanisms of Chelating Agents with Barium Sulfate In Presence Of Catalyst

4.2. Multi Stage Removal of Barite Filter Cake Weighted Water Based Drilling Fluid.

5. Accepted Conference Papers

5.1. Ba Geri B.S, Al-Mutairi, S.H. and Mahmoud, M.A., **2013,** Different Techniques for Characterizing the Filter Cake, **SPE- 163960**, presented at the SPE Middle East Unconventional Gas Conference & Exhibition in Muscat, Sultanate of Oman, 28–30 January.

5.2. Ba Geri, B.S., Al-Majed, A., Al-Mutairi, S.H., Ul-Hamid, A. and Sultan, A., **2013**, Evaluation of Filter Cake Mineralogy in Extended Reach and Maximum Reservoir Contact Wells in Sandstone Reservoirs, **SPE-163519**, presented at the SPE / IADC Drilling Conference and Exhibition in Amsterdam, The Netherlands, 05–07 March.

5.3. Ba Geri, B.S., and Mahmoud, M.A., **2013**. A New Diversion Technique to Remove the Formation Damage from Maximum Reservoir Contact and Extended Reach Wells in Sandstone Reservoirs. Paper **SPE 165163** presented at the SPE European Formation Damage Conference & Exhibition, Noordwijk, The Netherlands, 5-7 June.

5.4. Ba Geri, B.S., Anifowose, F.A, Abdulraheem, A., **2015**. Artificial Intelligence Based Estimation of Water Saturation Using Electrical Measurements Data in a Carbonate Reservoir, Paper **SPE 172564-MS** presented at the SPE Middle East Oil & Gas Show and Conference, Manama, Bahrain, 8-11 March

5.5. **Ba Geri, B.S.,** Mahmoud, M. Sultan, A., A., Al-Mutairi, S. H., Abdulraheem, A., **2015**. Effect of the Drilled Cuttings on Filter Cake Sealing Properties and Internal Invasion Depth in MRC wells. Paper **SPE-175168-MS** presented at the SPE Kuwait Oil & Gas Show and Conference held in Mishref, Kuwait, 11–14 October.

5.6. **Ba Geri, B.S.,** Mahmoud, M.A., Al-Mutairi, S.H., Abdulraheem, A., **2015**. Porosity and Permeability profile of filter Cake in horizontal wells and their impact on filter cake removal. Paper **SPE/ IPTC-18465-MS** presented at the International Petroleum Technology Conference held in Doha, Qatar, 7–9 December.

5.7. Mahmoud, M. A., Kamal, M., **Ba Geri, B. S.**, Hussein, I., **2015**. Removal of Pyrite and Different Types of Iron Sulfide Scales in Oil and Gas Wells without H2S Generation. Paper **SPE/ IPTC-18279-MS** presented at the International Petroleum Technology Conference held in Doha, Qatar, 7–9 December.

5.8. ***Ba Geri, B.S.,*** Mahmoud, M. A., *Al-Majed, A., Al-Mutairi, and* Abdulraheem, A., **2017**. *Water Base Barite Filter Cake Removal Using Non-Corrosive Agents.* Prepared for presentation at ***MEOS 2017.*** *SPE Paper Number:* ***SPE-183653-MS***

Ministry of Education
King Fahd University of Petroleum & Minerals
DEPARTMENT OF PETROLEUM ENGINEERING
(036)

وزارة التعليم
جامعة الملك فهد للبترول و المعادن
قسم هندسة البترول
(٠٣٦)

Memorandum

Date : October 12, 2016

To : **Dr. Badr Salem Bageri**

Subject : **Congratulations on Completing your PhD Defense**

Greetings!

The Department of Petroleum Engineering would like to congratulate you for successful completion of your education and most importantly along with degree of PhD in Petroleum Engineering. You truly have proved your self-dedication and perseverance that indeed brought you this level of success! The Department is proud of your accomplishment and performance during the MS and PhD degrees. You were the first PhD student who started with idea three-years back and it's today a field-trial along with excellent record of publications. You have set the bar-high for other Yemeni students. Please rest assured that you have the department support in all your endeavors and we hope to hear many more stories of your success in the future.

Thank you,

تحياتي

Dr. Abdullah S. Sultan
Chairman, Petroleum Engineering Department

cc: Dean, College of Petroleum Engineering & Geosciences
Dean, Graduate Studies
Student's Advisor
Dissertation Committee Members
Graduate Coordinator
Student's file

Att: Student's Record of Publications

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